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(54) CLEANING LIQUID FOR SUBSTRATE FOR SEMICONDUCTOR DEVICE AND CLEANING METHOD

(57)Abstract:
PROBLEM TO BE SOLVED: To provide cleaning liquid and a cleaning method by which minute particles or an organic contaminant stuck on the surface of a substrate can be removed by cleaning without corroding the surface of the substrate and the surface thereof in highly cleaned in the substrate for a semiconductor device.
SOLUTION: The cleaning liquid for the substrate for a semiconductor device contains at least following elements (A), (B) and (C), and the cleaning method using the cleaning liquid is used. The element (A) is an ethylene oxide type surfactant that has a hydrocarbon group and polyoxyethylene that may have a substituent (excluding phenyl group) and wherein the ratio (m/n) of the carbon number (m) in the hydrocarbon group to the oxyethylene number in the polyoxyethylene group is 1 to 1.5, the carbon number (m) is 9 or more, and the oxyethylene number (n) is 7 or more, the element (B) is water, and the element (C) is an alkaline or an organic acid.

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CLAIMS

[Claim(s)]

[Claim 1] The penetrant remover of the substrate for semiconductor devices characterized by containing the following components (A), (B), and (C) at least.

component (A): — the hydrocarbon group and polyoxyethylene radical which may have the substituent (except for a phenyl group) — having — the carbon number in a hydrocarbon group (m), and the oxyethylene in a polyoxyethylene radical — the ratio (m/n) of the base (n) — 1-1.5 — it is — a carbon number (m) — 9 or more and oxyethylene — the ethyleneoxide mold surfactant whose base (n) is seven or more.

(Component B): Water component (C): Alkali or an organic acid [claim 2] The penetrant remover according to claim 1 whose carbon numbers (m) in a component (A) are 9-16.

[Claim 3] The penetrant remover according to claim 1 or 2 whose pH alkali is contained as a component (C) and is nine or more.

[Claim 4] The penetrant remover according to claim 3 whose component (C) is the alkali compound expressed with the following general formulas (I).

[Formula 1] (R1)4N+OH- (I)

(However, R1 shows a hydrogen atom or a hydroxyl group, an alkoxy group, and the alkyl group that may be permuted with the halogen, and even if the whole of R1 is the same, it may differ.)

[Claim 5] The penetrant remover according to claim 4 whose component (C) is the 4th class ammonium of hydroxylation which has the alkyl group and/or hydroxyalkyl radical of ammonium hydroxide or carbon numbers 1-4.

[Claim 6] The penetrant remover according to claim 1 or 2 whose pH an organic acid is contained as a component (C) and is 1-5.

[Claim 7] The penetrant remover according to claim 6 whose components (C) are an organic carboxylic acid and/or an organic sulfonic acid.

[Claim 8] The penetrant remover according to claim 7 whose organic carboxylic acid is at least one sort chosen from the group which consists of an acetic acid, a propionic acid, oxalic acid, a succinic acid, a malonic acid, a citric acid, a tartaric acid, and a malic acid.
[Claim 9] The penetrant remover according to claim 7 whose organic sulfonic acid is at least one sort chosen from the group which consists of methansulfonic acid, ethane sulfonic acid, n-propane sulfonic acid, i-propane sulfonic acid, and n-butane sulfonic acid.
[Claim 10] A penetrant remover given in any of claims 1-9 whose contents of a component (A) are 0.0001 - 1 % of the weight they are.
[Claim 11] A penetrant remover given in any of claims 1-10 whose components (A) are polyoxyethylene alkyl ether they are.
[Claim 12] Furthermore, a penetrant remover given in any of claims 1-11 containing a complexing agent they are.
[Claim 13] A penetrant remover given in any of claims 1-12 which do not contain a hydrogen peroxide substantially they are.
[Claim 14] The washing approach of the substrate for semiconductor devices characterized by using a penetrant remover given in any of claims 1-13 they are.
[Claim 15] The washing approach according to claim 14 which washes a substrate while irradiating a supersonic wave with a frequency of 0.5MHz or more.
[Claim 16] The washing approach according to claim 14 or 15 which carries out brush washing of the substrate for semiconductor devices after carrying out chemical mechanical polishing.
[Claim 17] The washing approach given in any of claims 14-16 which warm and use a penetrant remover for the temperature of 40-70 degrees C they are.
[Claim 18] after washing by the penetrant remover — further — heat-treatment with a temperature of 300 degrees C or more — or the washing approach according to claim 14 of performing ozone water treatment.
[Claim 19] The washing approach according to claim 14 applied to the substrate for semiconductor devices with which the contact angle of water has an insulator layer 60 degrees or more on a front face.
[Claim 20] The washing approach according to claim 14 applied to the substrate for semiconductor devices which has silicon, transition metals, or a transition-metals compound on a front face.
[Claim 21] The substrate penetrant remover for semiconductor devices which is characterized by filling the following conditions (a), (b), and (c) and which has a semiconductor device electrode or metal wiring on a front face at least.

(a) Don't corrode a semiconductor device electrode and metal wiring substantially.
(b) When the amount of contamination metals washes the substrate which are 1000-5000 (x1010 atoms/cm2), the amount of contamination metals after washing is below ten (x1010 atoms/cm2).
(c) [when the approximate circle configuration substrate front face of the radius r which has particle with a particle size of 0.1 micrometers or more 8000-100000 (an individual / 0.03m2) is washed between t (minute)] The particle number within the periphery on the substrate front face which makes a substrate and a core the same is 800/t or less piece within the periphery of periphery radius 0.6r after washing within 200/t or less piece or the periphery of periphery radius 0.9r in the case of t=0.5-1.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the penetrant remover used for washing on front faces of a substrate, such as the semi-conductor with which metal contamination and particle contamination pose a problem, glass, a metal, ceramics, resin, the magnetic substance, and a superconductor, about the penetrant remover and the washing approach of the substrate for semiconductor devices. detailed — this invention — quantity — it is related with the penetrant remover and the washing approach for washing the substrate front face for semiconductor devices in the process which manufactures the substrates for semiconductor devices a semiconductor device, for display devices, etc. that a pure substrate front face is required.

[0002] Especially the penetrant remover and the washing approach of this invention Semiconductor materials, such as silicon, Insulating materials, such as silicon nitride, silicon oxide, glass, and a low dielectric constant (Low-k) ingredient, In the substrate for semiconductor devices which has transition metals or a transition-metals compound all over surface [a part of] Organic contamination of a minute particle (particle) like the silica particle adhering to a substrate front face, an alumina particle, and an organic substance particle, resist residue, etc. and metal contamination are removed and combined, and the reattachment is controlled, and it can defecate to altitude, without causing the dry area and corrosion on the front face of a substrate.

[0003]

[Description of the Prior Art] At the production process of semiconductor devices, such as flat-panel displays, such as TFT liquid crystal, a microprocessor, memory, and CCD, pattern formation and thin film formation are performed on substrate front faces, such as

silicon, silicon oxide (SiO2), and glass, with the dimension of submicron one thru/or a quarter micron. Therefore, in each process of these manufactures, the slight contamination on the front face of a substrate concerned is also removed, and it has been a very important technical problem to defecate a substrate front face to altitude. Also in contamination, especially the particle contamination and metal contamination that are minute contamination are difficult to remove the all. However, in order for electrical characteristics and the yield of a semiconductor device to fall by this contamination, before carrying such contamination into degree process, it is necessary to remove as much as possible. And generally washing on the front face of a substrate by the penetrant remover is carried out to removal of such contamination.

[0004] In recent years, in manufacture of a semiconductor device, much more improvement in a throughput and production increase in efficiency are demanded. And about the substrate for semiconductor device manufacture which is in detailed-izing and a high integration inclination increasingly, it excels not only in the removal nature of the particle contamination on the front face of a substrate, and metal contamination but in the reattachment tightness after removal, and the penetrant remover and the washing approach of defecating a substrate front face to altitude quickly are desired.

[0005] Generally, it is known as a penetrant remover used for removal of particle contamination that an alkaline water solution is effective. Alkaline water solutions, such as an aqueous ammonia solution, a potassium-hydroxide water solution, and a tetramethylammonium hydroxide water solution, are used for washing on the front face for semiconductor devices of a substrate. Moreover, washing (it is called "SC-1 washing" or "APM washing".) by the penetrant remover (it is called "SC-1 penetrant remover" or an "APM penetrant remover".) containing ammonia, a hydrogen peroxide, and water is also used widely (for example, nonpatent literature 1 reference).

[0006] And recently, that the engine performance of such an alkaline penetrant remover should be improved, etching on the front face for semiconductor devices of a substrate is specifically controlled, a surface dry area is controlled, and the wettability on the front face of a substrate is also raised, and adding various surfactants to an alkaline penetrant remover for the purpose of raising the removal nature of particle contamination etc. is proposed variously.

[0007] For example, in order to control the dry area on the front face of a substrate by the penetrant remover, a surfactant is added in an alkaline hydrogen-peroxide-solution solution, and making the contact angle of the penetrant remover to a substrate front face into 10 or less degrees is proposed (for example, patent reference 1 reference). Moreover, in order to raise the wettability of the penetrant remover on the front face of a

substrate, the hydrogen-peroxide content alkalinity penetrant remover which added the ethyleneoxide addition type non-ion system surfactant whose numbers of addition mols of ethyleneoxide are 3-10 is proposed (for example, patent reference 2 reference).

[0008] Moreover, in order to control etching of the front face of the silicon substrate which is a typical semiconductor device substrate, adding various surfactants to an alkaline penetrant remover is proposed (for example, patent reference 3 reference). In order to raise the removal engine performance of organic substance contamination especially, the penetrant remover used for washing of the substrate for semiconductor devices containing a specific surface active agent is proposed (for example, patent reference 4 reference). For the reason on a decontamination disposition, adding alkylbenzene sulfonic acid to a hydrogen-peroxide content alkalinity penetrant remover is also proposed (for example, patent reference 5 reference). Moreover, for the reason on a particle removal disposition, adding the fluorochemical surfactant which consists of a fluoro alkyl sulfonamide compound to an APM penetrant remover is also proposed (for example, patent reference 6 reference).

[0009] Moreover, in washing of the substrate for semiconductor devices, an acid penetrant remover is also useful in addition to the alkaline above-mentioned penetrant remover. Generally, although the acid penetrant remover is effective in the metal decontamination on the front face of a substrate, adding various surfactants also to an acid penetrant remover for the purpose of the removal disposition top of particle contamination etc. is proposed from it being unsuitable for removal of particle contamination. For example, washing a silicon wafer using a specific surfactant and a specific hydrofluoric acid is proposed (for example, patent reference 7 reference).

[0010] Moreover, adding a surfactant and ozone in the fluoric acid water solution used for washing of a silicon wafer is proposed (for example, patent reference 8 reference). Adding an organic-acid compound to a dispersant and/or a surfactant is also proposed for removal of the metal impurity which stuck to the substrate which has metal wiring on a front face, and particle contamination (for example, patent reference 9 reference).

[0011] Moreover, virgin metal group ingredients, such as copper (Cu) and a tungsten (W), are newly being introduced with detailed-izing and quantity lamination of a semiconductor device in recent years as wiring (only henceforth "wiring") and the metallic material used for the electrode (only henceforth an "electrode") in a semiconductor device which connects between the minute semiconductor devices in a semiconductor device. Specifically as a wiring material, Cu with low resistance is being adopted from the aluminum (aluminum) which was used from the former and to which it came.

[0012] Moreover, the interlayer insulation film between the semiconductor devices which have a laminated structure is mentioned as other new ingredients. The low dielectric constant film which used the film which consists of the organic polymer ingredient and inorganic polymer ingredient with a dielectric constant lower than SiO2 film currently used from the former as this interlayer insulation film is being adopted. Among the production process of a semiconductor device, in case this interlayer insulation film is the washing process (it may be hereafter called a "back process") of the substrate performed after metal wiring is formed in that front face, it is exposed on a substrate with wiring.

[0013] Moreover, a tungsten is being introduced into an electrode as an electrode material with it. [low resistance and] [advantageous to micro processing] In case an electrode is the washing process (it may be hereafter called a "last process") of the substrate before metal wiring formation, it is usually exposed on a substrate front face. Since all the substrate front faces washed in a last process consisted of Si compounds conventionally and a semiconductor device was affected also for slight contamination, the substrate front face needed to be defecated to altitude. Therefore, powerful washing by RCA washing was indispensable.

[0014] In recent years, adaptation of various proposals which carried out point ** is tried that a substrate which an exotic material which was mentioned above has exposed to a front face should be washed to altitude.

[0015]

[Nonpatent literature 1] W. Kern and D.A.Puotinen: RCA Review, p.187, June [(1970) patent reference 1] JP,5-335294,A [the patent reference 2] The patent No. 3169024 official report [the patent reference 3] JP,2001-40389,A [the patent reference 4] JP,11-121418,A [the patent reference 5] JP,7-245281,A [the patent reference 6] JP,5-251416,A [the patent reference 7] JP,7-216392,A [the patent reference 8] JP,8-69990,A [the patent reference 9] JP,2001-7071,A [0016]

[Problem(s) to be Solved by the Invention] At the conventional back process which used aluminum wiring, since the effect of metal contamination was low compared with that aluminum wiring is weak to strong acid or a strong base, and a last process, only easy washing by ultrapure water or the organic solvent was performed. However, when Cu was used instead of aluminum, the two following problems newly arose.

[0017] In the first place, in the first place, Cu was one of the pollutants disliked most for Si, its diffusion rate of Cu in the oxide film on the front face of a semiconductor device (SiO2 film) was quick, and it had become a problem to exceed aluminum you to be Haruka whenever [bad influence].

[0018] The point that second dry etching cannot do Cu unlike aluminum is a problem. the approach of performing Cu plating to the insulator layer which trenched, forming wiring beforehand (in order forming Cu wiring), and subsequently shaving off a garbage by approaches, such as CMP (Chemical Mechanical Polishing), in order to form wiring by Cu, and the so-called DAMASHIN — wiring formation by law must be carried out.

[0019] It poses a problem that the polish particle in the slurry used for a lot of Cu and CMP (particle represented by the aluminum oxide particle etc.) pollutes Cu wiring and a low dielectric constant film front face with the wiring formation by the above-mentioned DAMASHIN method. By easy washing by ultrapure water or the organic solvent, the contamination on such a front face of a substrate could not be removed, but has already been a serious problem.

[0020] When the conventional RCA washing by strong acid or the strong base was performed to the above contamination, the problem of dissolving to a hydrogen peroxide had newly produced virgin metal group ingredients, such as Cu and W. And further, since a low dielectric constant film front face is hydrophobicity, the wettability of a penetrant remover is bad, and crawls a penetrant remover, and it has the problem of being [fully] especially hard to remove removal of particle contamination.

[0021] Therefore, at the washing process of a substrate of having the above exotic materials on a front face, serious problems — it will become impossible to wash [which used the RCA penetrant remover containing hydrogen peroxide solution] from now on — have arisen, and in washing the substrate which has a weak virgin metal group ingredient on a front face in drug solutions, such as a hydrogen peroxide, development of a new penetrant remover is desired strongly.

[0022] On the other hand, the development of the penetrant remover which contains a surfactant like which mentioned above has been made. However, there was no penetrant remover which reattachment prevention is fully made and is satisfied with following the (1) - (3) of the technical problem of a publication with metal decontamination and particle decontamination by this, and it had become a technical problem in the surface washing of a substrate.

[0023] (1) a room temperature or warming — sometimes, cause neither washing performance degradation nor the residual of the oil droplet on the front face of a substrate, without a surfactant's serving as an oil droplet and doing deposit and nebula of into a penetrant remover.

(2) Fizz be small and don't have a bad influence on actuation of a washing station.

(3) A surfactant is the matter which does not have a bad influence on natural

environment, and washing waste fluid can process appropriately.

[0024] For example, since an anion system surfactant generally does not have a cloudy point, a high cleaning effect is expected, and it can use the temperature of a penetrant remover, making it high (for example, 80 degrees C or more). However, since it is high fizz, there is a possibility of having a bad influence on the operability in a washing station.

[0025] Moreover, a non-ion system surfactant has the high washing engine performance, and although it is low fizz, generally a cloudy point is low. Therefore, when a high cleaning effect is expected and it washes by making temperature of a penetrant remover high, this surfactant appears as the shape of an oil droplet in a penetrant remover, and there is a problem of remaining on a substrate.

[0026]

[Means for Solving the Problem] this invention persons examined wholeheartedly the substrate penetrant remover for semiconductor devices which uses a surface active agent about the technical problem mentioned above. Its attention was paid to the surface active agent especially used for a penetrant remover, and the ethyleneoxide mold surface active agent which is especially a non-ion system surface active agent.

[0027] An ethyleneoxide mold surface active agent has a hydrocarbon group and a polyoxyethylene radical in the same molecular structure. the ratio (m/n) of the carbon number (m) by which this invention persons are contained in a hydrocarbon group in the ethyleneoxide mold surface active agent of such structure, and the number of the oxyethylene radicals in a polyoxyethylene radical (n) — 1-1.5, and a carbon number (m) — the oxyethylene in 9 or more and a polyoxyethylene radical — the base (n) paid its attention to the surface active agent of specification within the limits which fulfills seven or more conditions.

[0028] Under a room temperature and the condition of atmospheric pressure, many of ethyleneoxide mold surfactants of this specification within the limits are solid-states, and its solubility to water is low. Therefore, such an ethyleneoxide mold surfactant was dealt with in the industrial production process, the sex was low and use was avoided. However, a hydrogen peroxide was not contained unexpectedly and substantially but, as for the substrate penetrant remover for semiconductor devices containing the alkali or the organic acid which was made to carry out heating melting, was dissolved in water, and prepared such an ethyleneoxide mold surfactant of specific within the limits, ** also showed the good washing engine performance. From the general contamination cleaning effect, it especially excelled in the detergency (particle removal nature of particle-size the order of 0.1 micrometers) over minute particle contamination which

cannot be predicted. And the above-mentioned substrate penetrant remover for semiconductor devices tended to crawl an aquosity penetrant remover for hydrophobicity, and did so the cleaning effect which showed sufficient wettability also to the low dielectric constant film front face where particle removal nature is low, and was excellent to it. this invention persons came to complete a header and this invention for these things.

[0029] That is, the summary of this invention consists in the washing approach which uses the penetrant remover and the penetrant remover concerned of the substrate for semiconductor devices characterized by containing the following components (A), (B), and (C) at least.

[0030] component (A): — the hydrocarbon group and polyoxyethylene radical which may have the substituent (except for a phenyl group) — having — the carbon number in a hydrocarbon group (m), and the oxyethylene in a polyoxyethylene radical — the ratio (m/n) of the base (n) — 1-1.5 — it is — a carbon number (m) — 9 or more and oxyethylene — the ethyleneoxide mold surfactant whose base (n) is seven or more.

(Component B): Water component (C): Alkali or an organic acid [0031]

[Embodiment of the Invention] Hereafter, this invention is explained to a detail. At least, the penetrant remover of this invention contains water as a specific surfactant and a component (B) as a component (A), and contains alkali or an organic acid as a component (C).

[0032] the hydrocarbon group and polyoxyethylene radical on which the surfactant used as a component (A) may have the substituent (except for a phenyl group) in this invention — having — the carbon number in a hydrocarbon group (m), and the oxyethylene in a polyoxyethylene radical — the ratio (m/n) of the base (n) — 1-1.5 — it is — a carbon number (m) — 9 or more and oxyethylene — the base (n) is the ethyleneoxide mold surfactant which is seven or more.

[0033] When the above-mentioned ratio (m/n) is less than one, it becomes inadequate corrosion controlling [of particle removal capacity or silicon] in liquid. Moreover, the load of the soluble fall to the water by the increase of oxyethylene chain length and waste fluid processing also increases. On the other hand, when exceeding 1.5, the emulsion of an O/W mold is formed in lye at the time of washing, and a surfactant serves as a fine oil droplet, it deposits and becomes cloudy, and problems, such as washing performance degradation and a residual of an oil droplet, are caused. Ratios (m/n) are 1-1.4 preferably.

[0034] When the above-mentioned carbon number (m) is less than nine, even if a ratio (m/n) is said optimal within the limits, particle removal nature falls. Moreover, when

(m) is too large, since the soluble fall to water and the load of waste fluid processing also increase, it is not desirable. therefore, a carbon number (m) — desirable — 9-16 — it is 10-14 still more preferably. However, in case the hydrocarbon group which constitutes a component (A) has a hydrocarbon group as a substituent, it sets to m the total number of the carbon number in the hydrocarbon group used as a principal chain, and the hydrocarbon group which is a substituent.

[0035] Moreover, when the above-mentioned (n) is less than seven, even if a ratio (m/n) is said optimal within the limits, particle removal nature falls. When (n) is too large, the load of waste fluid processing becomes large, and it becomes easy to disassemble a surfactant in a penetrant remover. therefore, (n) — desirable — 7-16 — it is 7-14 still more preferably.

[0036] By using the above-mentioned ethyleneoxide mold surface active agent specified by this invention, both the wettability of a penetrant remover and the removal nature of particle become good. As the above-mentioned ethyleneoxide mold surface active agent, polyoxyethylene alkyl ether, polyoxyethylene fatty acid ester, polyoxyethylene alkylamine, a polyoxyethylene-alkyl-ether sulfate, etc. are mentioned, for example. The polyoxyethylene alkyl ether especially expressed with the following general formula (II) from viewpoints, such as the removal nature of particle contamination and reattachment prevention ability, is desirable.

[0037]

[Formula 2] R2O-(CH2CH2O)nH (II)

(However, R2 shows a hydroxyl group, the amino group, an alkoxy group, and the alkyl group that may be permuted with the halogen, the carbon number (m) contained in an alkyl group is nine or more, and (n) expresses seven or more numbers.)

[0038] As an example of the above-mentioned polyoxyethylene alkyl ether The polyoxyethylene (n= 8) nonyl ether, the polyoxyethylene (n= 9) DESHIRU ether, The polyoxyethylene (n= 11) undecyl ether, the polyoxyethylene (n= 10) lauryl ether, The polyoxyethylene (n= 11) lauryl ether, the polyoxyethylene (n= 10) tridecyl ether, The polyoxyethylene (n= 12) tridecyl ether, the polyoxyethylene (n= 11) tetradecyl ether, The polyoxyethylene (n= 13) tetradecyl ether, the polyoxyethylene (n= 12) pentadecyl ether, The polyoxyethylene (n= 14) pentadecyl ether, the polyoxyethylene (n= 12) cetyl ether, the polyoxyethylene (n= 15) cetyl ether, the polyoxyethylene (n= 18) oleyl ether, etc. are mentioned. In addition, the numeric value in the above-mentioned n expresses n in the aforementioned general formula (II).

[0039] In this invention, as long as it is within the limits of this invention, two or more ethyleneoxide mold surfactants with which (m) differs from (n) may be used together at

a rate of arbitration. if the average of 9 or more and (n) fulfills [the average of (m/n) of all surfactants / the average of 1-1.5, and (m)] seven or more conditions in case two or more more sorts of surfactants are used together — the surfactant according to each individual — setting (m/n) — it may be over less than 1.0 and 1.5, or (m) may be less than nine and (n) may be less than seven.

[0040] The content of the component in a penetrant remover (A) is usually 0.001 - 0.05 % of the weight especially preferably 0.001 to 0.1% of the weight still more preferably 0.0003 to 0.5% of the weight preferably 0.0001 to 1% of the weight. When the concentration of a component (A) is too low, the particle decontamination engine performance is not enough, on the other hand, when the concentration of a component (A) is too high, it may become unsuitable for a washing process, and the load in the case of there being no change in the removal engine performance of particle contamination, and foaming becoming remarkable, and carrying out biodegradation processing of the waste fluid may increase.

[0041] In the gestalt usually sold, metal impurities of 1 - about 1000 ppm of numbers, such as Na, K, and Fe, may contain the component (A). In this case, a component (A) serves as a metal pollution source. Therefore, as for the surfactant used as a component (A), it is desirable to refine and use it. and the content of each metal impurity — usually — 10 ppm or less 1 ppm or less are preferably set to 0.1 ppm or less still more preferably. The method of dipping in ion exchange resin and, for example, making resin catch a metal impurity as the purification approach, after dissolving a surfactant with water is suitable.

[0042] By using the component (A) refined as mentioned above, the penetrant remover by which the metal impurity content was reduced extremely can be obtained. Especially as a penetrant remover of this invention, it is desirable among the metal impurities in a penetrant remover that 5 or less ppb of contents of Na, Mg, aluminum, K, calcium, Fe, Cu, Pb, and Zn is 0.1 or less ppb also in 20 or less ppb at least.

[0043] In addition, in this invention, surfactants other than a component (A) may be used in the range which does not spoil the effectiveness of this invention. As surface active agents other than a component (A), any of a cation system surface active agent, an anion system surface active agent, and the Nonion system surface active agent are sufficient. using an anion system surfactant and the Nonion system surfactant especially — good — better ** — concrete — as for example, an anion system surfactant — ARUKI of carbon numbers 8-12 A RUBENZEN sulfonic acid and its salt, and alkyl methyl taurine acid of carbon numbers 8-12 and the salt, the alkyl-sulfuric-acid ester of carbon numbers 8-12, its salt, etc. mention — having — **. As an Nonion system surfactant, it is

****** which consists only of polyoxyalkylene. A sex agent etc. is mentioned.

[0044] In this invention, water is used as a component (B). quantity — the case where he wants to obtain a pure substrate front face — usually — deionized water — ultrapure water is used preferably. Moreover, the hydrogen water which made hydrogen gas dissolved in the electrolysis ion water obtained by the electrolysis of water and water can also be used.

[0045] In this invention, alkali or an organic acid is used as a component (C). That is, let the penetrant remover of this invention be an alkaline penetrant remover or an acid penetrant remover.

[0046] Although especially the class of alkali used by this invention is not limited, as typical alkali, ammonium hydroxide (aqueous ammonia solution) and organic alkali are mentioned. As organic alkali, amines, such as the 4th class ammonium of hydroxylation, an amine, and amino alcohol, are mentioned. What has a hydroxyl group, an alkoxy group, the alkyl group of the carbon numbers 1-4 which may be permuted with the halogen, or the hydroxyalkyl radical of carbon numbers 1-4 as the 4th class ammonium of hydroxylation is desirable, and even if all of these substituents are the same, they may differ.

[0047] As above alkyl groups, the low-grade alkyl group of the carbon numbers 1-4, such as a methyl group, an ethyl group, a propyl group, and butyl, is mentioned, and the low-grade hydroxyalkyl radical of the carbon numbers 1-4, such as a hydroxymethyl group, a hydroxyethyl radical, a hydroxypropyl radical, and hydroxy butyl, is mentioned as a hydroxyalkyl radical.

[0048] As an example of the 4th class ammonium of hydroxylation of having the above-mentioned substituent, tetramethyl AMONIUMU hydroxide (TMAH), tetraethylammonium hydroxide, TORIMECHIRU (hydroxyethyl) ammonium hydroxide (common name: choline), triethyl (hydroxyethyl) ammonium hydroxide, etc. are mentioned. On the other hand, ethylenediamine, monoethanolamine, trimethano RUAMIN, etc. are mentioned as amines.

[0049] In above-mentioned alkali, the ammonium hydroxide from the reasons of that there are few cleaning effects and metal residuals, economical efficiency, the stability of a penetrant remover, etc., tetramethylammonium hydroxide (TMAH), and TORIMECHIRU (hydroxyethyl) ammonium hydroxide (common name: choline) are desirable. Such alkali may be used independently and two or more sorts may be used for it at a rate of arbitration.

[0050] Although what is necessary is just to choose the concentration of the alkali in a penetrant remover suitably, it is desirable that it is the concentration from which pH of a

penetrant remover becomes nine or more alkalinity. The decontamination effectiveness which alkali concentration is too low, and is the purpose of this invention when pH is not high may not be acquired. On the other hand, since the danger that about [being economically disadvantageous] and a substrate front face will be damaged by etching, without acquiring the effectiveness by having raised pH when pH is too high increases, it is not desirable. therefore, pH of an alkaline penetrant remover — desirable — 9-13 — further — desirable — 10-12.5 — it is 10.5-12 especially preferably.

[0051] Although especially the class of organic acid used by this invention is not limited, an organic carboxylic acid or its organic sulfonic acid is desirable. As a typical thing of an organic carboxylic acid, formic acid, an acetic acid, a propionic acid, butanoic acid, an isobutyric acid, a valeric acid, ethyl methylacetic acid, trimethylacetic acid, oxalic acid, a succinic acid, a malonic acid, a citric acid, a tartaric acid, a malic acid, etc. are mentioned. In these, one sort chosen from the group of an acetic acid, a propionic acid, oxalic acid, a succinic acid, a malonic acid, a citric acid, a tartaric acid, and a malic acid or two sorts or more are desirable, and one sort chosen from the group of an acetic acid, oxalic acid, and a citric acid or two sorts or more are still more desirable. An acetic acid is the most desirable at the point that are used for the etchant ingredient of a semi-conductor substrate etc., and an object with few metal impurities can be cheap, can obtain by the high grade by distillation actuation, and generating of the fine particles by moisture evaporation does not take place, either.

[0052] As a typical thing of an organic sulfonic acid, methansulfonic acid, ethane sulfonic acid, n-propane sulfonic acid, i-propane sulfonic acid, n-butane sulfonic acid, a phenyl sulfonic acid, etc. are mentioned. In these, methansulfonic acid and/or ethane sulfonic acid are desirable, and especially methansulfonic acid is desirable. The above-mentioned organic acid may be used independently and two or more sorts may be used for it at a rate of arbitration.

[0053] Although what is necessary is just to choose the concentration of the organic acid in a penetrant remover suitably, it is desirable that it is the concentration from which pH of an acid penetrant remover is set to 1-5. The removal or the antisticking effectiveness of contamination which the concentration of an organic acid is too low, and are the purpose of this invention when pH is not sufficiently low may not be acquired. On the other hand, when concentration is too high, it is economically disadvantageous, without acquiring the effectiveness by having reduced pH, and since it can also become the cause of the corrosion on about [that it is] and the front face of a substrate, it is not desirable. pH of an acid penetrant remover is 2-3 preferably.

[0054] In the penetrant remover of this invention, since the front face which reduced

further the metal contamination on the front face of a substrate and which was extremely defecated by altitude will be obtained if a complexing agent is made to contain, it is desirable. As a complexing agent, the thing of well-known arbitration can be used conventionally. What is shown by the following (1) - (4) is mentioned that what is necessary is to judge the class of complexing agent synthetically and just to choose it from the contamination level on the front face of a substrate, a metaled class, the cleanliness level required of a substrate front face, complexing agent cost, chemical stability, etc.

[0055] The compound which has the nitrogen, carboxyl group, and/or phosphonic acid radical which are a donor atom : (1) For example Amino acid, such as a glycine; Imino 2 acetic acid, nitrilotriacetic acid, ethylenediaminetetraacetic acid [EDTA], A transformer -1, 2-diamino cyclohexane 4 acetic acid [CyDTA], Nitrogen-containing carboxylic acids, such as diethylenetriamine pentaacetic acid [DTPA] and triethylenetetramine 6 acetic acid [TTHA]; Ethylenediamine tetrakis (methylene phosphonic acid) [EDTPO], Nitrogen-containing phosphonic acid, such as NITORIRO tris (methylene phosphonic acid) [NTPO] and a propylenediamine tetrapod (methylene phosphonic acid) [PDTMP], is mentioned.

[0056] (2) Phenols, such as compound:, for example, a catechol, which has the OH radical and/or two O-radicals or more which were coupled directly with the carbon atom which has an aromatic hydrocarbon ring and constitutes an aromatic hydrocarbon ring, resorcinol, and tiron, the derivative of those, etc. are mentioned.

[0057] (3) Compound having the above (1) and the structure of

(2) : [0058] An ethylenediamine JIORUTO hydroxyphenyl acetic acid [EDDHA] and its derivative : (3-1) For example An ethylenediamine JIORUTO hydroxyphenyl acetic acid [EDDHA], Ethylenediamine-N, N'-screw [(2-hydroxy-5-methylphenyl) acetic-acid] [EDDHMA], Ethylenediamine-N, N'-screw [(2-hydroxy-5-KURORU phenyl) acetic-acid] [EDDHCA], an ethylenediamine-N and N'-screw — aromatic series nitrogen-containing carboxylic-acids; ethylenediamine-N, such as [(2-hydroxy-5-sulfophenyl) an acetic acid [EDDHSA]], and N' - screw [(2-hydroxy-5-methylphenyl) phosphonic acid] — Aromatic series nitrogen-containing phosphonic acid, such as an ethylenediamine-N and N'-screw [(2-hydroxy-5-phospho phenyl) phosphonic acid], is mentioned.

[0059] N, N'-bis(2-hydroxybenzyl) ethylenediamine-N, N'-2 acetic-acid [HBED], and its derivative : (3-2) For example N, N'-bis(2-hydroxybenzyl) ethylenediamine-N, N'-2 acetic-acid [HBED], N, N'-bis(2-hydroxy-5-methylbenzyl) ethylenediamine-N, N'-2 acetic-acid [HMBED], N, N'-bis(2-hydroxy-5-KURORU benzyl) ethylenediamine-N,

N'-2 acetic acid, etc. are mentioned.

[0060] (4) In addition, hydrogen halides, such as carboxylic-acids; hydrofluoric acids, such as amines; formic acids, such as :, for example, ethylenediamine, an eight quinolinol, and o-phenanthrolin, an acetic acid, oxalic acid, and a tartaric acid, a hydrochloric acid, a hydrogen bromide, and hydrogen iodide, those salts; oxo acid, such as a phosphoric acid and condensed phosphoric acid, those salts, etc. are mentioned.

[0061] The thing of the gestalt of an acid may be used for the above-mentioned complexing agent, and the thing of the gestalt of salts, such as ammonium salt, may be used for it.

[0062] the inside of the complexing agent mentioned above — nitrogen-containing phosphonic acid; ethylenediamine JIORUTO hydroxyphenyl acetic acids [EDDHA], such as nitrogen-containing carboxylic-acids; ethylenediamine tetrakis (methylene phosphonic acid) [EDTPO], such as ethylenediaminetetraacetic acid [EDTA] and diethylenetriamine pentaacetic acid [DTPA], and a propylenediamine tetrapod (methylene phosphonic acid) [PDTMP], and derivative;N of those from the reasons of a cleaning effect, chemical stability, etc., and N' - bis(2-hydroxybenzyl) ethylenediamine-N and N' -2 acetic acid [HBED] is desirable.

[0063] inside — **** — a cleaning effect — a viewpoint — from — Ellen — diamine — JIORUTO — hydroxyphenyl — an acetic acid — [— EDDHA —] — ethylenediamine - N — N — ' - a screw — [(2-hydroxy-5-methylphenyl) — an acetic acid —] — [— EDDHMA —] — diethylenetriamine pentaacetic acid — [— DTPA —] — ethylenediaminetetraacetic acid — [— EDTA —] — propylenediamine — a tetrapod (methylene phosphonic acid) — [— PDTMP —] — being desirable . The above-mentioned complexing agent may be used independently and two or more sorts may be used for it at a rate of arbitration.

[0064] Although what is necessary is just to choose the concentration of the complexing agent in a penetrant remover as arbitration with the class of contamination metal impurity, an amount, and the cleanliness level required of a substrate front face, it is 1-10000 ppm usually 10-200 ppm still more preferably 5-1000 ppm preferably. When the concentration of a complexing agent is too low, the decontamination or the antisticking effectiveness by the complexing agent are not acquired, but a complexing agent adheres to about [being economically disadvantageous] and a substrate front face, without acquiring the effectiveness of balancing the increment in concentration, when too high, and the danger of remaining after surface treatment increases.

[0065] In addition, since the complexing agent contains metal impurities, such as FeAl of 1 - about 1000 ppm of numbers, and Zn, in the reagent usually sold, it can consider the case where the complexing agent used by this invention serves as a metal pollution

source. Although these metals form a complexing agent and a stable complex and exist in early stages, if a complexing agent decomposes while carrying out long duration use as a surface penetrant remover, they will separate and will adhere to a substrate front face. Therefore, as for the complexing agent used by this invention, it is desirable to use it, refining beforehand. and the content of each metal impurity contained — usually — 5 ppm or less 1 ppm or less are preferably set to 0.1 ppm or less still more preferably. As the purification approach, after dissolving a complexing agent in acidity or an alkaline solution for example, filtration separation is carried out and an insoluble impurity is removed, and it neutralizes again, a crystal is deposited, and the method of separating the crystal concerned with liquid is suitable.

[0066] Moreover, the penetrant remover of this invention may contain other components at a rate of arbitration in the range which does not spoil the engine performance. as other components — a sulfur-containing organic compound (2-mercapto thiazoline —) 2-mercapto imidazoline, 2-mercaptoethanol, the thioglycerol, etc., a nitrogen-containing organic compound (benzotriazol and alkyl benzotriazol —) A tetra-SOL, 3-aminotriazole, N3 (R is the alkyl group of carbon numbers 1-4) (R), N(ROH) 3 (R is the alkyl group of carbon numbers 1-4), urea, thiourea, etc., A water-soluble polymer (a polyethylene glycol, polyvinyl alcohol, etc.), Anticorrosives, such as an alkyl alcoholic system compound (ROH (R is the alkyl group of carbon numbers 1-4)), The etching accelerator which can expect the removal effectiveness, such as a polymer which adhered firmly, is mentioned after dry etching, such as dissolved gas, such as reducing agents, such as acids, such as a sulfuric acid and a hydrochloric acid, and a hydrazine, hydrogen, an argon, and nitrogen, fluoric acid, ammonium fluoride, and BHF.

[0067] And oxidizers, such as a hydrogen peroxide, ozone, and oxygen, are also mentioned as other components which the penetrant remover of this invention is made to contain. In the washing process of the substrate for semiconductor devices, in case a silicon (BEASHIRIKON) substrate front face without an oxide film is washed, since the surface dry area by etching to a substrate front face can be stopped by combination of an oxidizing agent, it is desirable. When making the alkaline penetrant remover of this invention contain a hydrogen peroxide, hydrogen-peroxide concentration in a penetrant remover is usually preferably made into 0.1 - 1 % of the weight 0.01 to 5% of the weight.

[0068] By the way, wiring of a semiconductor device and the device component electrode which consist of a metallic material which reacts with a hydrogen peroxide and dissolves may be exposed to the front face of the substrate to wash. As such a

metallic material, transition metals or transition-metals compounds, such as Cu and W, are mentioned, for example. Under the present circumstances, as for the penetrant remover used for washing, it is desirable not to contain a hydrogen peroxide substantially. The penetrant remover of this invention shows sufficient washing engine performance, without having a bad influence on such a metallic material, even if it does not contain a hydrogen peroxide substantially unlike the conventional APM penetrant remover.

[0069] In addition, in the penetrant remover of this invention, it means not producing bad influences, such as corrosion, deterioration, etc. by the hydrogen peroxide, to wiring materials and electrode materials, such as the ingredient on the substrate washed saying "a hydrogen peroxide is not contained substantially", for example, Cu, and W, and the low dielectric constant film. That is, when these ingredients consider as a semiconductor device, it means fully functioning as wiring, an electrode, etc. For that purpose, it is so desirable that the content is stopped few even if a hydrogen peroxide is not contained in the penetrant remover of this invention, and it makes and being contained. the content — for example, 1 ppm 10 ppm or less are preferably set to 10 or less ppb still more preferably.

[0070] The penetrant remover of this invention is used for washing on front faces of a substrate, such as the semi-conductor with which metal contamination and particle contamination pose a problem, glass, a metal, ceramics, resin, the magnetic substance, and a superconductor. especially — quantity — it is used suitable for washing on the front face for semiconductor devices of a substrate in the process which manufactures the substrates for semiconductor devices a semiconductor device, for display devices, etc. with which a pure substrate front face is demanded. Wiring, an electrode, etc. may exist in the front face of these substrates. As an ingredient of wiring or an electrode, metals, such as insulating material;W, such as semiconductor material;SiO(s)2, such as Si, germanium, and GaAs, silicon nitride, glass, a low dielectric constant ingredient, an aluminum oxide, transition-metals oxide (titanium oxide, tantalum oxide, an oxidization hafnium, zirconium dioxide, etc.), TiO(Ba, Sr) 3 (BST), polyimide, and organic thermosetting resin, and Cu, aluminum, or these alloys, silicide, a nitride, etc. are mentioned. A low dielectric constant ingredient is the generic name of the ingredient whose specific inductive capacity is 3.5 or less. Incidentally, the specific inductive capacity of SiO2 is 3.8-3.9.

[0071] Especially the penetrant remover of this invention is used suitable for washing of the substrate for semiconductor devices which has transition metals or a transition-metals compound on a front face. As transition metals, W, Cu, Ti, Cr, Co, Zr,

Hf, Mo, Ru, Au, Pt, Ag, etc. are mentioned, and the CHITSU ghost of these transition metals, an oxide, silicide, etc. are mentioned as a transition-metals compound. In these, W and/or Cu are desirable.

[0072] As a process which washes the substrate which has a tungsten, washing on the front face of a substrate which has a gate electrode, silicon, etc. at the time of using a tungsten as a gate electrode material is mentioned to a front face. Specifically, the washing process after forming the tungsten film in a semiconductor device, the washing process after carrying out dry etching of the tungsten film especially, and the washing process after carrying out an ion implantation to a silicon outcrop after that are mentioned.

[0073] If the penetrant remover of this invention is used, even if it performs neither ultrasonic irradiation nor a brush scrub, a particle metallurgy group is removable. Therefore, the penetrant remover of this invention is suitable for washing of a gate electrode and a substrate front face when a possibility of breaking if ultrasonic cleaning and a brush scrub are performed forms a very detailed (for example, the width of face of a gate electrode is about 0.15 micrometers) large gate electrode with a tungsten.

[0074] As a process which washes the substrate which has Cu, washing on the front face of a substrate which has Cu wiring, an interlayer insulation film, etc. at the time of using Cu as a wiring material is mentioned to a front face. Specifically, the washing process after forming Cu film in a semiconductor device especially the washing process after performing CMP (Chemical Mechanical Polishing) to Cu film, and the washing process after opening a hole in the interlayer insulation film on wiring by dry etching are mentioned.

[0075] Moreover, the penetrant remover of this invention is used suitable also for washing of the substrate for semiconductor devices which has a low dielectric constant ingredient used as an interlayer insulation film ingredient on a front face. As a low dielectric constant ingredient, it is roughly divided into three with an organic polymer ingredient, an inorganic polymer (siloxane system) ingredient, and a porosity (porous) ingredient. As an organic polymer ingredient, Polyimide, BCB (Benzocyclobutene), Flare (Honeywell), SiLK (Dow Chemical), etc. are mentioned, and FSG (Fluorinated silicate glass), BLACK DIAMOND (Applied Materials), Aurora (Japan ASM), etc. are mentioned as an inorganic polymer ingredient.

[0076] The penetrant remover of this invention is used suitable for the surface washing of the substrate for semiconductor devices irrespective of the existence of the electrode in a substrate front face, or a wiring material as mentioned above. Also in it, the penetrant remover of this invention is used suitable for washing of the substrate for

semiconductor devices which the contact angle of the water in a substrate front face shows hydrophobicity 60 degrees or more.

[0077] The preparation approach of the penetrant remover of this invention should just be conventionally based on a well-known approach. Any 2 components or three components or more in the constituent (for example, accepting a surfactant, ammonium hydroxide, water, and the need other components, such as a complexing agent) of a penetrant remover may be blended beforehand, the remaining components may be mixed after that, and all may be mixed at once.

[0078] As mentioned above, also with the substrate for semiconductor devices which has a metallic material with low resistance in a front face to drug solutions, such as a future exotic material, i.e., a hydrogen peroxide etc., since the substrate penetrant remover for semiconductor devices of this invention does not corrode these exotic materials substantially, it turns into an usable penetrant remover which does the outstanding cleaning effect so at both a last process and a back process.

[0079] That is, other summaries of this invention consist in the substrate penetrant remover for semiconductor devices which is characterized by filling the following conditions (a), (b), and (c) and which has a semiconductor device electrode or metal wiring on a front face at least.

[0080] (a) Don't corrode a semiconductor device electrode and metal wiring substantially.

(b) When the amount of contamination metals washes the substrate which are 1000-5000 (x1010 atoms/cm2), the amount of contamination metals after washing is below ten (x1010 atoms/cm2).

(c) [when the approximate circle configuration substrate front face of the radius r which has particle with a particle size of 0.1 micrometers or more 8000-100000 (an individual / 0.03m2) is washed between t (minute)] The particle number within the periphery on the substrate front face which makes a substrate and a core the same is 800/t or less piece within the periphery of periphery radius 0.6r after washing within 200/t or less piece or the periphery of periphery radius 0.9r in the case of t=0.5-1.

[0081] In addition, a convention of the above-mentioned (b) and (c) is not what specified the property of the penetrant remover of this invention and specified the washing conditions for which the penetrant remover of this invention is used. Moreover, in the penetrant remover of this invention, semiconductor device electrode metallurgy group wiring on the substrate washed saying "a semiconductor device electrode and metal wiring are not corroded substantially", and when it does not produce bad influences, such as corrosion and deterioration, and these ingredients specifically

consider as a semiconductor device to electrode materials and wiring materials, such as W and Cu, it means fully functioning as an electrode, wiring, etc.

[0082] In the penetrant remover of above-mentioned this invention, filling conditions (b) and (c) shows that it is possible to fully remove metal contamination, particle contamination, and any contamination.

[0083] In case the candidate for washing is the front face of an approximate circle tabular substrate, i.e., an approximate circle configuration substrate front face, even if conditions (c) are short-time washing, they do not call at the location on the front face of a substrate, but mean that a substrate front face can be defecated to altitude. that is, the approximate circle configuration substrate front face of the radius r which has particle with a particle size of 0.1 micrometers or more 8000-100000 (an individual / 0.03m2) — a part for washing time amount t:0.5 - 1[—] — ******, after washing Within the periphery of periphery radius 0.6r on the substrate front face made the same which is the inner circumference section comparatively, a substrate and a core Particle is made into 800/t or less piece also into the periphery of periphery radius 0.9r which removes the particle which remains to 200/t or less piece, and contains even the periphery section comparatively, and it means that a substrate front face can be defecated to altitude.

[0084] moreover, it can set to the substrate penetrant remover for semiconductor devices of this invention mentioned above — "— the case where it washes — setting — " — it is shown by the washing approach which is mentioned later that it is the case where a penetrant remover washes the substrate for semiconductor devices. The washing approach will not usually be limited, especially if it is the approach which may be adopted at the time of washing of the substrate for semiconductor devices. Especially, the contact approach to the substrate of a penetrant remover makes a penetrant remover on a substrate the spin type which carries out high-speed rotation of the substrate with a sink, and since the result by which considering as the range of room temperature -90 degree C was stabilized is obtained, whenever [solution temperature / of a penetrant remover] is desirable.

[0085] Furthermore, since the washing result of having been stabilized more by adopting mechanical cleaning, such as scrub washing which used the washing approach by physical force, for example, a washing brush, ultrasonic cleaning which irradiates a supersonic wave with a frequency of 0.5MHz or more at a substrate, the washing approach which uses these together, etc. is obtained in the case of washing, it is desirable.

[0086] The washing approach of this invention is performed by the approach of contacting a penetrant remover to a substrate directly. The DIP type which a penetrant

remover is filled [type] to a cleaning tank and makes a substrate immersed in the contact approach to the substrate of a penetrant remover, the spin type which carries out high-speed rotation of the substrate for a penetrant remover with a sink on a substrate from a nozzle, the spray ceremony which sprays and washes liquid at a substrate are held. There are a batch type washing station which washes to coincidence two or more substrates held in the cassette as equipment for performing such washing, a single-wafer-processing washing station which equips an electrode holder with one substrate and washes it.

[0087] In the case of a batch type washing station, in the case of a single-wafer-processing washing station, washing time amount is usually 5 minutes from 5 seconds preferably from 1 second from 30 seconds for 15 minutes for 1 to 15 minutes for 30 minutes. When too long [when washing time amount is too short, a cleaning effect is not enough, and], the improvement in a cleaning effect is small and causes the fall of a throughput. Although the penetrant remover of this invention is applicable to any above-mentioned approach, it is preferably used for washing of a spin type or a spray type from the point which can perform more efficient decontamination for a short time. And if compaction of ** and washing time amount and reduction of the amount of the penetrant remover used apply to the single-wafer-processing washing station which poses a problem, since these problems are solved, it will be desirable.

[0088] Although temperature of a penetrant remover is usually made into a room temperature, it is the purpose which raises a cleaning effect and it is desirable to warm at about 40-70 degrees C. Furthermore, when washing the substrate which silicon has exposed to a front face, in order that organic substance contamination may tend to remain on a silicon front face, it is desirable to offer and carry out the pyrolysis of the substrate to heating down stream processing with a temperature of 300 degrees C or more, or to carry out the oxidative degradation place of the organic substance by ozone water treatment.

[0089] Moreover, as for the washing approach of this invention, it is desirable to make it use together with mechanical cleaning, such as scrub washing which used the washing approach by physical force, for example, a washing brush, or ultrasonic cleaning. If ultrasonic irradiation or a brush scrub is especially used together, since the removal nature of particle contamination improves further and leads also to compaction of washing time amount, it will be desirable. It is desirable to wash by washing after CMP especially using the brush made of resin.

[0090] Although the quality of the material of the brush made of resin can be chosen as arbitration, it is desirable to use PVA (polyvinyl alcohol), for example. Moreover, if a

supersonic wave with a frequency of 0.5MHz or more is irradiated at a substrate, since the removal nature of particle improves remarkably according to a synergism with a surface active agent, it will be desirable. Furthermore, washing by the electrolysis ion water obtained by the electrolysis of water or the hydrogen water which made hydrogen gas dissolved in water may be combined before the washing approach of this invention, and/or with the back.

[0091]

[Example] Next, it is not limited by the following examples unless this invention exceeds the summary according to an example, although this invention is explained concretely.

[0092] The 8 inch silicon substrate (disc-like substrate whose radius r is 4 inches) examples 1 and 2 and the example 1 of a comparison - with 3 (detergency evaluation of the particle contamination by scrub type washing) low dielectric constant film (SiOC: carbon content SiO2) was immersed in the SiO2 slurry solution for 10 minutes. The substrate after immersion was rinsed for 1 minute with ultrapure water, and spin desiccation was carried out with the multi-spinner (Made in Khai Joe "KSSP-201"). Then, it checked that measured the particulate number adhering to a substrate front face, and SiO2 particle 0.2 micrometers or more had adhered more than fixed quantity (however, an upper limit 100000 pieces) with laser surface-analysis equipment ("LS-5000" by Hitachi Electronics Engineering).

[0093] The penetrant remover shown in Table 1 was used, with the above-mentioned multi-spinner, brush scrub washing of the above-mentioned SiO2 particle adhesion substrate was carried out with the brush made from PVA, and particle was removed. Washing by the penetrant remover was performed for 1 minute at the room temperature. Then, after ultrapure water washed the substrate for 1 minute, spin desiccation was carried out and the washed substrate was obtained. A result is shown in Table 1.

[0094]

[Table 1]

[0095] examples 3-6 and the examples 4-8 (detergency evaluation of the particle contamination by scrub type washing) of a comparison — the SiO2 particle adhesion substrate was first created like the example 1. Subsequently, the penetrant remover shown in Table 2 was used, except having set washing time amount as for 0.5 minutes, the SiO2 particle adhesion substrate was washed like the example 1, and the washed substrate was obtained. A result is shown in Table 2.

[0096] Wettability evaluation in Table 2 was performed by the following approach. Namely, it soaks at right angles to each penetrant remover given [the piece of a test (2cm angle) with the low dielectric constant film (SiOC: carbon content SiO2)] in Table 2. The piece of a test was perpendicularly pulled out after 0.5 minutes, and the rate of area that the penetrant remover to the whole surface product of the piece of a test was attached estimated. The valuation basis was made into more than O:80%, less than [more than **:50%80%], and less than [x:50%].

[0097]

[Table 2]

	洗浄剤成分									濡れ性	付着粒子数 0.2μm以上：個／ウエーハ	
	界面活性剤					アルカリ		錯化剤				
	構造式	m	n	m/n	濃度 ppm	種類	濃度 ppm	種類	濃度 ppm		洗浄前	洗浄後
実施例3	$C_{12}H_{25}O(C_2H_4O)_9H$	12	9	1.3	50	TMAH	50	EDDHA	100	○	>8000	1321
実施例4	$C_{12}H_{25}O(C_2H_4O)_{11}H$	12	11	1.1	50	TMAH	50	EDDHA	100	○		1012
実施例5	$C_{13}H_{27}O(C_2H_4O)_{10}H$	13	10	1.3	50	TMAH	50	EDDHA	100	○		1123
実施例6	$C_{16}H_{33}O(C_2H_4O)_{13}H$	16	13	1.2	50	TMAH	50	EDDHA	100	○		1524
比較例4	$C_8H_{17}O(C_2H_4O)_8H$	8	8	1.0	50	TMAH	50	EDDHA	100	×		4924
比較例5	$C_{12}H_{25}O(C_2H_4O)_7H$	12	7	1.7	50	TMAH	50	EDDHA	100	×		2061
比較例6	$C_{12}H_{25}O(C_2H_4O)_{13}H$	12	13	0.9	50	TMAH	50	EDDHA	100	×		1712
比較例7	$C_{16}H_{33}O(C_2H_4O)_{20}H$	16	20	0.8	50	TMAH	50	EDDHA	100	○		1776
比較例8	$C_{18}H_{37}O(C_2H_4O)_{20}H$	18	20	0.9	50	TMAH	50	EDDHA	100	△		2926

洗浄方法：スクラブ式洗浄（洗浄温度：室温，洗浄時間ｔ：０．５分）
測定装置：日立電子エンジニアリング社製「ＬＳ－５０００」（エッジカット：１０ｍｍ）
洗浄前の基板表面上のパーティクル個数は８０００～１００００００［個／０．０３m^2］である。
洗浄後のパーティクル個数は基板と中心を同じくする半径０．９ｒの円周内での個数である。

[0098] After carrying out surface treatment of the 8 inch silicon substrate (disc-like substrate whose radius r is 4 inches) an example 7 - with 10 (detergency evaluation of the particle contamination by scrub type washing) low dielectric constant film (SiOC: carbon content SiO2) for 1 minute by fluoric acid 0.5% of the weight, it was immersed in the SiO2 slurry solution for 10 minutes. The substrate after immersion was rinsed for 1 minute with ultrapure water, and spin desiccation was carried out with the multi-spinner (Made in Khai Joe "KSSP-201"). Then, the particulate number which adhered to the substrate front face with laser surface-analysis equipment ("LS-6600" by Hitachi Electronics Engineering) was measured, and it checked that SiO2 particle 0.11 micrometers or more had adhered more than fixed quantity (however, an upper limit 100000 pieces).

[0099] The penetrant remover shown in Table 3 was used, with the above-mentioned multi-spinner, brush scrub washing of the above-mentioned SiO2 particle adhesion substrate was carried out with the brush made from PVA, and particle was removed. Washing by the penetrant remover was performed for 0.5 minutes at the room temperature. Then, after ultrapure water washed the substrate for 1 minute, spin

desiccation was carried out and the washed substrate was obtained. A result is shown in Table 3.

[0100]

[Table 3]

	洗浄剤成分											洗浄剤pH	付着粒子数 0.11μm以上：個／ウエーハ	
	界面活性剤					アルカリ		酸		錯化剤				
	構造式	m	n	m/n	濃度 ppm	種類	濃度 ppm	種類	濃度 ppm	種類	濃度 ppm		洗浄前	洗浄後
実施例7	$C_{12}H_{25}O(C_2H_4O)_{11}H$	12	11	1.1	50	TMAH	75	−	−	EDDHA	100	10.5	>20000	838
実施例8	$C_{12}H_{25}O(C_2H_4O)_{11}H$	12	11	1.1	200	TMAH	1000	−	−	EDDHA	100	12		792
実施例9	$C_{12}H_{25}O(C_2H_4O)_{11}H$	12	11	1.1	50	−	−	酢酸	0.45	−	−	2.5		497
実施例10	$C_{12}H_{25}O(C_2H_4O)_{11}H$	12	11	1.1	200	−	−	酢酸	0.45	−	−	2.5		813

洗浄方法：スクラブ式洗浄（洗浄温度：室温，洗浄時間ｔ：０．５分）
測定装置：日立電子エンジニアリング社製「ＬＳ－６６００」（エッジカット：１０ｍｍ）
洗浄前の基板表面上のパーティクル個数は２００００～１００００００［個／０．０３m^2］である。
洗浄後のパーティクル個数は基板と中心を同じくする半径０．９ｒの円周内での個数である。

[0101] examples 11 and 12 and the example 9 (detergency evaluation of the particle contamination by scrub type washing) of a comparison — the SiO2 particle adhesion substrate was first created like the example 1. Subsequently, the penetrant remover shown in Table 4 was used, except having set washing time amount as for 0.5 minutes, the SiO2 particle adhesion substrate was washed like the example 1, and the washed substrate was obtained. A result is shown in Table 4.

[0102]

[Table 4]

	洗浄剤成分							付着粒子数 0.2μm以上：個／ウエーハ	
	界面活性剤					酸			
	構造式	m	n	m/n	濃度 ppm	種類	濃度 wt%	洗浄前	洗浄後
実施例11	$C_{12}H_{25}O(C_2H_4O)_{11}H$	12	11	1.1	50	酢酸	2.25	>8000	248
実施例12	$C_{12}H_{25}O(C_2H_4O)_{11}H$	12	11	1.1	50	クエン酸	10		290
比較例1	デモールAS	-	-	-	10000	クエン酸	10		2455

デモールAS：β－ナフタリンスルホン酸ホルマリン縮合物
洗浄方法：スクラブ式洗浄（洗浄温度：室温，洗浄時間t：0．5分）
測定装置：日立電子エンジニアリング社製「LS－5000」（エッジカット：40mm）
洗浄前の基板表面上のパーティクル個数は8000～100000［個／0．03m²］である。
洗浄後のパーティクル個数は基板と中心を同じくする半径0．6rの円周内での個数である。

[0103] The 4 inch silicon substrate (disc-like substrate whose radius r is 2 inches) to which the thermal oxidation film with a thickness of about 100nm was attached to the example 13 and the example of comparison 10 substrate front face was exposed into atmospheric air for 3 hours, and the suspended matter in mind was made to adhere. As a result of measuring with substrate surface-analysis equipment ("LS-5000" by Hitachi Electronics Engineering), particle with a particle size of 0.2 micrometers or more was carrying out 10,000 or more (however, upper limit 100000 pieces) piece adhesion at the base. the stream by the pure water during 10 minutes after carrying out immersion processing of this substrate for 10 minutes each at each penetrant remover given in Table 3 by which temperature control was carried out to 50 degrees C — it washed and dried with the spin dryer. The measurement result of the number of particle which remains on the substrate after washing processing is shown in Table 5.

[0104] In example of comparison 11 example 13, except having used the solution (APM penetrant remover) which mixed an ammonium hydroxide water solution, 50-% of the weight hydrogen peroxide solution, and ultrapure water by the capacity factor 1:4:20 29% of the weight, and was prepared as a penetrant remover, it carried out like the example 13 and evaluated. A result is shown in Table 5.

[0105] Although the penetrant remover of the example 11 of a comparison has comparatively few adhesion particle numbers after washing, since a hydrogen peroxide is included in a penetrant remover, it cannot perform application to a future exotic material, but becomes unusable in the future.

[0106]

[Table 5]

	洗浄剤成分							洗浄剤pH	付着粒子数 0.2μm以上：個／ウエーハ	
	界面活性剤					アルカリ				
	構造式	m	n	m/n	濃度 ppm	種類	濃度 ppm		洗浄前	洗浄後
実施例13	$C_{12}H_{25}O(C_2H_4O)_{11}H$	12	11	1.1	25	NH_4OH	2800	11.3	>10000	756
比較例10	-	-	-	-	-	NH_4OH	2800	11.3		1866
比較例11	-	-	-	-	-	APM	6000	10.3		1145

APM：29重量%アンモニア水、30重量%過酸化水素水および純水を容量比1：2：40で混合した溶液
洗浄温度：50℃、洗浄時間t：10分（エッジカット：10mm）

[0107] The substrate from which immersion processing of the 4 inch silicon substrate (disc-like substrate whose radius r is 2 inches) to which an example 14 and the example 12 of a comparison - 14 natural oxidation film were attached was carried out for 5 minutes 0.5% of the weight at HF water solution, and the scaling film was removed was obtained. the stream carry out immersion processing of this for 10 minutes at each penetrant remover given in Table 4 by which Silicon(IV) Nitride particle (product made from Johnson Matthey "Stk#12145") 0.02 g/L was added, and temperature control was carried out to 50 degrees C, and according to after and the pure water during 5 minutes — it washed and dried with the spin dryer. With substrate surface-analysis equipment ("LS-5000" by Hitachi Electronics Engineering), the number of particle with a particle size of 0.2 micrometers or more which remains on the substrate after washing processing was measured. A result is shown in Table 6.

[0108]

[Table 6]

	洗浄液成分							洗浄液pH	付着粒子数 0.2μm以上：個／ウエーハ
	界面活性剤					アルカリ			
	構造式	m	n	m/n	濃度 ppm	種類	濃度 ppm		浸漬処理後
実施例14	$C_{12}H_{25}O(C_2H_4O)_{11}H$	12	11	1.1	25	NH_4OH	2800	11.3	296
比較例12	アデカＬ－４４	-	-	-	25	NH_4OH	2800	11.3	3888
比較例13	ユニセーフDC1100	-	-	-	25	NH_4OH	2800	11.3	3208
比較例14	-	-	-	-	-	NH_4OH	2800	11.3	>10000

旭電化工業社製「アデカＬ－４４」：オキシエチレン及びオキシプロピレンのブロック共重合体，分子量2200
日本油脂社製「ユニセーフＤＣ1100」：オキシエチレン及びオキシプチレンのブロック共重合体，分子量1100
処理温度：５０℃、処理時間ｔ：１０分（エッジカット：１０mm）

[0109] The 4 inch silicon substrate (disc-like substrate whose radius r is 2 inches) which removed the surface natural oxidation film was prepared for the example 15 and the 15,160.5 % of the weight HF water solution of examples of a comparison by carrying out immersion processing for 5 minutes. the stream by the pure water during 5 minutes after carrying out predetermined time immersion processing of this at a penetrant remover given in each table 5 by which temperature control was carried out — it washed and dried with the spin dryer. after substrate desiccation — immediately — an atomic force microscope (Nano ScopeIIIa made from Digital Instruments) — the Z-axis on the front face of a substrate — Rms (nm) which is the standard deviation of a variation rate was measured. A result is shown in Table 7.

[0110] It is a deed about evaluation according to viewing about the surface dry area of the above-mentioned substrate. The following result was obtained. That is, in the case of the examples 15 and 16 of a comparison, a surface dry area like the interference fringe covering countless crater-like irregularity with a diameter of about about 1-10mm and the whole substrate front face was observed on the substrate front face, but in the case of the example 15, it was not observed.

[0111]

[Table 7]

	洗浄液成分							洗浄液 pH	処理温度 (℃)	処理時間 (分)	Rms (nm)
	界面活性剤					アルカリ					
	構造式	m	n	m/n	濃度 ppm	種類	濃度 ppm				
実施例 15	$C_{12}H_{25}O(C_2H_4O)_{11}H$	12	11	1.1	25	NH_4OH	2800	11.3	50	10	0.281
比較例 15	-	-	-	-	-	NH_4OH	2800	11.3	40	10	4.328
比較例 16	-	-	-		-	NH_4OH	2800	11.3	50	10	3.074

処理温度：４０℃又は５０℃、処理時間ｔ：１０分

[0112] The piece of a test of the polycrystal polish recon of about 100nm of thickness which removed the scaling film was prepared for examples 16-19 and the 17 - 190.5 % of the weight HF water solution of examples of a comparison by carrying out immersion processing for 5 minutes. the stream by the pure water during 5 minutes after carrying out immersion processing of this piece of a test for 10 minutes at each penetrant remover given in Table 6 by which temperature control was carried out to 50 degrees C — it washed and dried by the nitrogen blow. The thickness of polycrystal polish recon was measured with the optical interference type thickness measurement vessel (the "nano spec. L-6100" by the nano metrics company). The etching rate was computed from the thickness measurement before and behind washing processing. A result is shown in Table 8.

[0113]

[Table 8]

	洗浄液成分							洗浄液 pH	エッチングレート (nm／min)
	界面活性剤					アルカリ			
	構造式	m	n	m/n	濃度 ppm	種類	濃度 ppm		
実施例 16	$C_{12}H_{25}O(C_2H_4O)_{11}H$	12	11	1.1	5	NH_4OH	2800	11.3	0.48
実施例 17	$C_{12}H_{25}O(C_2H_4O)_{11}H$	12	11	1.1	10	NH_4OH	2800	11.3	0.52
実施例 18	$C_{12}H_{25}O(C_2H_4O)_{11}H$	12	11	1.1	25	NH_4OH	2800	11.3	0.43
実施例 19	$C_{12}H_{25}O(C_2H_4O)_{11}H$	12	11	1.1	100	NH_4OH	2800	11.3	0.34
比較例 17	-	-	-	-	-	NH_4OH	2800	11.3	6.26
比較例 18	ＰＥＧ４００	-	8.7	-	1000	NH_4OH	2800	11.3	2.69
比較例 19	ユニオックス M-400	1	8.4	0.1	1000	NH_4OH	2800	11.3	1.91

日本油脂社製「ＰＥＧ400」：オキシチレン縮合物，分子量400
日本油脂社製「ユニオックスM-400」：オキシチレン縮合物のモノメチルエーテル，分子量400
処理温度：５０℃、処理時間ｔ：１０分

[0114] The piece of a test of the tungsten of about 100nm of thickness which removed the scaling film was prepared for the example 20 and the 10.3 % of the weight aqueous ammonia solution of examples of reference by carrying out immersion processing for 5 minutes. the stream by the pure water during 5 minutes after carrying out immersion processing of this piece of a test for 10 minutes at each penetrant remover given in Table 9 by which temperature control was carried out to 40 degrees C — it washed and dried by the nitrogen blow. The thickness of a tungsten used total reflection fluorescence X rays (product made from Jeol "RIX-3000"), and drew them by the conversion from reflectivity. The etching rate was computed from the thickness measurement before and behind washing processing. A result is shown in Table 9.

[0115] Here, it turns out that an example 20 is compared with the example 1 of reference, and the penetrant remover of this invention controls the etching rate on the front face of a substrate to a mere alkali water solution, and it excels as a substrate penetrant remover for semiconductor devices the clear passage.

[0116] In example of comparison 20 example 20, except having used the same APM penetrant remover as the example 11 of a comparison as a penetrant remover, it carried out like the example 20 and evaluated. A result is shown in Table 9.

[0117]

[Table 9]

	洗浄液成分							洗浄液 pH	エッチングレート（ｎｍ／ｍｉｎ）
	界面活性剤					アルカリ			
	構造式	m	n	m/n	濃度 ppm	種類	濃度 ppm		
実施例 20	$C_{12}H_{25}O(C_2H_4O)_{11}H$	12	11	1.1	25	NH_4OH	2800	11.3	0.071
参考例 1	-	-	-	-	-	NH_4OH	2800	11.3	0.080
比較例 20	-	-	-	-	-	ＡＰＭ	6000	10.4	>10

ＡＰＭ：２９重量％アンモニア水、３０重量％過酸化水素水および純水を容量比１：２：４０で混合した溶液
処理温度：４０℃、処理時間ｔ：１０分

[0118] The example 21 and the 214 inches silicon substrate (disc-like substrate whose radius r is 2 inches) of examples of a comparison were immersed in the APM penetrant remover containing a metal ion (Fe, Cu). This APM penetrant remover mixed aqueous ammonia, 31-% of the weight hydrogen peroxide solution, and water by the capacity factor 1:1:5 29% of the weight, and it added and prepared the metal ion content water solution so that a metal content might serve as Fe (20ppb) and Cu (1 ppm) at this. The silicon substrate after immersion was rinsed for 10 minutes with ultrapure water, it dried by nitrogen blow, and the silicon substrate polluted with the metal was obtained.

[0119] The polluted silicon substrate and the silicon substrate after washing performed analysis of the contamination metal on this silicon substrate (Fe, Cu) by the following approach. That is, it collects by processing a substrate in the water solution which contains 0.1 % of the weight of fluoric acid, and 1 % of the weight of hydrogen peroxides for the metal in a substrate front face, the amount of metals is measured with an inductively-coupled-plasma-source-mass-spectrometry plan (ICP-MS), and it converts into the metal concentration (atoms/cm2) on the front face of a substrate.

[0120] The penetrant remover which shows washing of the above-mentioned silicon substrate polluted with the metal in Table 10 was used, and it considered as penetrant remover temperature [of 60 degrees C], and washing time amount 10 minutes, and carried out by the DIP type cleaning method. The analysis result of the polluted silicon substrate and the residual metal (Fe, Cu) of a washed silicon substrate surface are shown in Table 10.

[0121]

[Table 10]

	洗浄剤成分									金属除去性 濃度 ($\times 10^{10}$atoms/cm^2)	
	界面活性剤					アルカリ		錯化剤			
	構造式	m	n	m/n	濃度 ppm	種類	濃度 ppm	種類	濃度 ppm	Fe	Cu
実施例 21	$C_{12}H_{25}O(C_2H_4O)_{11}H$	12	11	1.1	50	TMAH	50	EDDHA	100	5.2	<1
比較例 21	-	-	-	-	-	TMAH	50	-	-	682	139
洗浄前（金属で汚染されたシリコンウェーハ）										1000～3000	3000～5000

洗浄方法：ディプ式洗浄
洗浄温度：６０℃，洗浄時間ｔ：１０分

[0122] It is clear from the above result the penetrant remover's of this invention to excel in the removal nature of the particle (particle) adhering to the low dielectric constant film which is hydrophobicity. Moreover, it compares with the conventional washing approach by the ammonium hydroxide solution or the APM solution, and it turns out that it has the more excellent removal nature also to the particle affix of the suspended matter origin in mind.

[0123] Similarly, even if a particle (particle) etc. mixes in a system, it becomes possible by removing by the washing approach of this invention to control adhesion in a substrate. Furthermore, it becomes as compared with the conventional washing approach, it is possible to control very small the roughness on the front face of silicon (front face that) also in an alkaline penetrant remover, and possible for there to be almost no side effects, such as polish recon and a processing dimensional change by etching to a tungsten, and to be compatible in detergency, roughness control, and low etching nature.

[0124] And even if the penetrant remover of this invention is a substrate for semiconductor devices which has an ingredient with low resistance in a front face to drug solutions, such as a hydrogen peroxide, it is clear to both a last process and a back process that it is the usable penetrant remover which does the outstanding cleaning effect so.

[0125]

[Effect of the Invention] According to the penetrant remover of this invention, in the substrate for semiconductor devices which has insulating materials, such as semiconductor materials, such as silicon, silicon nitride, silicon oxide, glass, and a low dielectric constant ingredient, transition metals, or a transition-metals compound all

over surface [a part of], also when washing removes effectively the particle (particle) adhering to a substrate front face, organic contamination, and metal contamination and a particle etc. mixes in a system, adhesion control is possible. Wettability of the hydrophobic low dielectric constant ingredient which is especially easy to crawl a drug solution is improved, and it excels in detergency. Moreover, it is possible for it to be compatible also in an alkaline penetrant remover in the roughness control on the front face of silicon and low etching nature in addition to detergency, and it is very useful industrially as the surface treatment approaches for [in production processes such as a semiconductor device and a display device,] contamination washing etc.

TECHNICAL FIELD

[Field of the Invention] This invention relates to the penetrant remover used for washing on front faces of a substrate, such as the semi-conductor with which metal contamination and particle contamination pose a problem, glass, a metal, ceramics, resin, the magnetic substance, and a superconductor, about the penetrant remover and the washing approach of the substrate for semiconductor devices. detailed — this invention — quantity — it is related with the penetrant remover and the washing approach for washing the substrate front face for semiconductor devices in the process which manufactures the substrates for semiconductor devices a semiconductor device, for display devices, etc. that a pure substrate front face is required.

[0002] Especially the penetrant remover and the washing approach of this invention Semiconductor materials, such as silicon, Insulating materials, such as silicon nitride, silicon oxide, glass, and a low dielectric constant (Low-k) ingredient, In the substrate for semiconductor devices which has transition metals or a transition-metals compound all over surface [a part of] Organic contamination of a minute particle (particle) like the silica particle adhering to a substrate front face, an alumina particle, and an organic substance particle, resist residue, etc. and metal contamination are removed and combined, and the reattachment is controlled, and it can defecate to altitude, without causing the dry area and corrosion on the front face of a substrate.

PRIOR ART

[Description of the Prior Art] At the production process of semiconductor devices, such as flat-panel displays, such as TFT liquid crystal, a microprocessor, memory, and CCD, pattern formation and thin film formation are performed on substrate front faces, such as silicon, silicon oxide (SiO2), and glass, with the dimension of submicron one thru/or a quarter micron. Therefore, in each process of these manufactures, the slight

contamination on the front face of a substrate concerned is also removed, and it has been a very important technical problem to defecate a substrate front face to altitude. Also in contamination, especially the particle contamination and metal contamination that are minute contamination are difficult to remove the all. However, in order for electrical characteristics and the yield of a semiconductor device to fall by this contamination, before carrying such contamination into degree process, it is necessary to remove as much as possible. And generally washing on the front face of a substrate by the penetrant remover is carried out to removal of such contamination.

[0004] In recent years, in manufacture of a semiconductor device, much more improvement in a throughput and production increase in efficiency are demanded. And about the substrate for semiconductor device manufacture which is in detailed-izing and a high integration inclination increasingly, it excels not only in the removal nature of the particle contamination on the front face of a substrate, and metal contamination but in the reattachment tightness after removal, and the penetrant remover and the washing approach of defecating a substrate front face to altitude quickly are desired.

[0005] Generally, it is known as a penetrant remover used for removal of particle contamination that an alkaline water solution is effective. Alkaline water solutions, such as an aqueous ammonia solution, a potassium-hydroxide water solution, and a tetramethylammonium hydroxide water solution, are used for washing on the front face for semiconductor devices of a substrate. Moreover, washing (it is called "SC-1 washing" or "APM washing".) by the penetrant remover (it is called "SC-1 penetrant remover" or an "APM penetrant remover".) containing ammonia, a hydrogen peroxide, and water is also used widely (for example, nonpatent literature 1 reference).

[0006] And recently, that the engine performance of such an alkaline penetrant remover should be improved, etching on the front face for semiconductor devices of a substrate is specifically controlled, a surface dry area is controlled, and the wettability on the front face of a substrate is also raised, and adding various surfactants to an alkaline penetrant remover for the purpose of raising the removal nature of particle contamination etc. is proposed variously.

[0007] For example, in order to control the dry area on the front face of a substrate by the penetrant remover, a surfactant is added in an alkaline hydrogen-peroxide-solution solution, and making the contact angle of the penetrant remover to a substrate front face into 10 or less degrees is proposed (for example, patent reference 1 reference). Moreover, in order to raise the wettability of the penetrant remover on the front face of a substrate, the hydrogen-peroxide content alkalinity penetrant remover which added the ethyleneoxide addition type non-ion system surfactant whose numbers of addition mols

of ethyleneoxide are 3-10 is proposed (for example, patent reference 2 reference).

[0008] Moreover, in order to control etching of the front face of the silicon substrate which is a typical semiconductor device substrate, adding various surfactants to an alkaline penetrant remover is proposed (for example, patent reference 3 reference). In order to raise the removal engine performance of organic substance contamination especially, the penetrant remover used for washing of the substrate for semiconductor devices containing a specific surface active agent is proposed (for example, patent reference 4 reference). For the reason on a decontamination disposition, adding alkylbenzene sulfonic acid to a hydrogen-peroxide content alkalinity penetrant remover is also proposed (for example, patent reference 5 reference). Moreover, for the reason on a particle removal disposition, adding the fluorochemical surfactant which consists of a fluoro alkyl sulfonamide compound to an APM penetrant remover is also proposed (for example, patent reference 6 reference).

[0009] Moreover, in washing of the substrate for semiconductor devices, an acid penetrant remover is also useful in addition to the alkaline above-mentioned penetrant remover. Generally, although the acid penetrant remover is effective in the metal decontamination on the front face of a substrate, adding various surfactants also to an acid penetrant remover for the purpose of the removal disposition top of particle contamination etc. is proposed from it being unsuitable for removal of particle contamination. For example, washing a silicon wafer using a specific surfactant and a specific hydrofluoric acid is proposed (for example, patent reference 7 reference).

[0010] Moreover, adding a surfactant and ozone in the fluoric acid water solution used for washing of a silicon wafer is proposed (for example, patent reference 8 reference). Adding an organic-acid compound to a dispersant and/or a surfactant is also proposed for removal of the metal impurity which stuck to the substrate which has metal wiring on a front face, and particle contamination (for example, patent reference 9 reference).

[0011] Moreover, virgin metal group ingredients, such as copper (Cu) and a tungsten (W), are newly being introduced with detailed-izing and quantity lamination of a semiconductor device in recent years as wiring (only henceforth "wiring") and the metallic material used for the electrode (only henceforth an "electrode") in a semiconductor device which connects between the minute semiconductor devices in a semiconductor device. Specifically as a wiring material, Cu with low resistance is being adopted from the aluminum (aluminum) which was used from the former and to which it came.

[0012] Moreover, the interlayer insulation film between the semiconductor devices which have a laminated structure is mentioned as other new ingredients. The low

dielectric constant film which used the film which consists of the organic polymer ingredient and inorganic polymer ingredient with a dielectric constant lower than SiO2 film currently used from the former as this interlayer insulation film is being adopted. Among the production process of a semiconductor device, in case this interlayer insulation film is the washing process (it may be hereafter called a "back process") of the substrate performed after metal wiring is formed in that front face, it is exposed on a substrate with wiring.

[0013] Moreover, a tungsten is being introduced into an electrode as an electrode material with it. [low resistance and] [advantageous to micro processing] In case an electrode is the washing process (it may be hereafter called a "last process") of the substrate before metal wiring formation, it is usually exposed on a substrate front face. Since all the substrate front faces washed in a last process consisted of Si compounds conventionally and a semiconductor device was affected also for slight contamination, the substrate front face needed to be defecated to altitude. Therefore, powerful washing by RCA washing was indispensable.

[0014] In recent years, adaptation of various proposals which carried out point ** is tried that a substrate which an exotic material which was mentioned above has exposed to a front face should be washed to altitude.

[0015]

[Nonpatent literature 1] W. Kern and D.A.Puotinen: RCA Review, p.187, June [(1970) patent reference 1] JP,5-335294,A [the patent reference 2] The patent No. 3169024 official report [the patent reference 3] JP,2001-40389,A [the patent reference 4] JP,11-121418,A [the patent reference 5] JP,7-245281,A [the patent reference 6] JP,5-251416,A [the patent reference 7] JP,7-216392,A [the patent reference 8] JP,8-69990,A [the patent reference 9] JP,2001-7071,A

EFFECT OF THE INVENTION

[Effect of the Invention] According to the penetrant remover of this invention, in the substrate for semiconductor devices which has insulating materials, such as semiconductor materials, such as silicon, silicon nitride, silicon oxide, glass, and a low dielectric constant ingredient, transition metals, or a transition-metals compound all over surface [a part of], also when washing removes effectively the particle (particle) adhering to a substrate front face, organic contamination, and metal contamination and a particle etc. mixes in a system, adhesion control is possible. Wettability of the hydrophobic low dielectric constant ingredient which is especially easy to crawl a drug solution is improved, and it excels in detergency. Moreover, it is possible for it to be

compatible also in an alkaline penetrant remover in the roughness control on the front face of silicon and low etching nature in addition to detergency, and it is very useful industrially as the surface treatment approaches for [in production processes such as a semiconductor device and a display device,] contamination washing etc.

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] At the conventional back process which used aluminum wiring, since the effect of metal contamination was low compared with that aluminum wiring is weak to strong acid or a strong base, and a last process, only easy washing by ultrapure water or the organic solvent was performed. However, when Cu was used instead of aluminum, the two following problems newly arose.

[0017] In the first place, in the first place, Cu was one of the pollutants disliked most for Si, its diffusion rate of Cu in the oxide film on the front face of a semiconductor device (SiO2 film) was quick, and it had become a problem to exceed aluminum you to be Haruka whenever [bad influence].

[0018] The point that second dry etching cannot do Cu unlike aluminum is a problem. the approach of performing Cu plating to the insulator layer which trenched, forming wiring beforehand (in order forming Cu wiring), and subsequently shaving off a garbage by approaches, such as CMP (Chemical Mechanical Polishing), in order to form wiring by Cu, and the so-called DAMASHIN — wiring formation by law must be carried out.

[0019] It poses a problem that the polish particle in the slurry used for a lot of Cu and CMP (particle represented by the aluminum oxide particle etc.) pollutes Cu wiring and a low dielectric constant film front face with the wiring formation by the above-mentioned DAMASHIN method. By easy washing by ultrapure water or the organic solvent, the contamination on such a front face of a substrate could not be removed, but has already been a serious problem.

[0020] When the conventional RCA washing by strong acid or the strong base was performed to the above contamination, the problem of dissolving to a hydrogen peroxide had newly produced virgin metal group ingredients, such as Cu and W. And further, since a low dielectric constant film front face is hydrophobicity, the wettability of a penetrant remover is bad, and crawls a penetrant remover, and it has the problem of being [fully] especially hard to remove removal of particle contamination.

[0021] Therefore, at the washing process of a substrate of having the above exotic materials on a front face, serious problems — it will become impossible to wash [which used the RCA penetrant remover containing hydrogen peroxide solution] from now on

— have arisen, and in washing the substrate which has a weak virgin metal group ingredient on a front face in drug solutions, such as a hydrogen peroxide, development of a new penetrant remover is desired strongly.

[0022] On the other hand, the development of the penetrant remover which contains a surfactant like which mentioned above has been made. However, there was no penetrant remover which reattachment prevention is fully made and is satisfied with following the (1) - (3) of the technical problem of a publication with metal decontamination and particle decontamination by this, and it had become a technical problem in the surface washing of a substrate.

[0023] (1) a room temperature or warming — sometimes, cause neither washing performance degradation nor the residual of the oil droplet on the front face of a substrate, without a surfactant's serving as an oil droplet and doing deposit and nebula of into a penetrant remover.

(2) Fizz be small and don't have a bad influence on actuation of a washing station.

(3) A surfactant is the matter which does not have a bad influence on natural environment, and washing waste fluid can process appropriately.

[0024] For example, since an anion system surfactant generally does not have a cloudy point, a high cleaning effect is expected, and it can use the temperature of a penetrant remover, making it high (for example, 80 degrees C or more). However, since it is high fizz, there is a possibility of having a bad influence on the operability in a washing station.

[0025] Moreover, a non-ion system surfactant has the high washing engine performance, and although it is low fizz, generally a cloudy point is low. Therefore, when a high cleaning effect is expected and it washes by making temperature of a penetrant remover high, this surfactant appears as the shape of an oil droplet in a penetrant remover, and there is a problem of remaining on a substrate.

MEANS

[Means for Solving the Problem] this invention persons examined wholeheartedly the substrate penetrant remover for semiconductor devices which uses a surface active agent about the technical problem mentioned above. Its attention was paid to the surface active agent especially used for a penetrant remover, and the ethyleneoxide mold surface active agent which is especially a non-ion system surface active agent.

[0027] An ethyleneoxide mold surface active agent has a hydrocarbon group and a polyoxyethylene radical in the same molecular structure. the ratio (m/n) of the carbon number (m) by which this invention persons are contained in a hydrocarbon group in

the ethyleneoxide mold surface active agent of such structure, and the number of the oxyethylene radicals in a polyoxyethylene radical (n) — 1-1.5, and a carbon number (m) — the oxyethylene in 9 or more and a polyoxyethylene radical — the base (n) paid its attention to the surface active agent of specification within the limits which fulfills seven or more conditions.

[0028] Under a room temperature and the condition of atmospheric pressure, many of ethyleneoxide mold surfactants of this specification within the limits are solid-states, and its solubility to water is low. Therefore, such an ethyleneoxide mold surfactant was dealt with in the industrial production process, the sex was low and use was avoided. However, a hydrogen peroxide was not contained unexpectedly and substantially but, as for the substrate penetrant remover for semiconductor devices containing the alkali or the organic acid which was made to carry out heating melting, was dissolved in water, and prepared such an ethyleneoxide mold surfactant of specific within the limits, ** also showed the good washing engine performance. From the general contamination cleaning effect, it especially excelled in the detergency (particle removal nature of particle-size the order of 0.1 micrometers) over minute particle contamination which cannot be predicted. And the above-mentioned substrate penetrant remover for semiconductor devices tended to crawl an aquosity penetrant remover for hydrophobicity, and did so the cleaning effect which showed sufficient wettability also to the low dielectric constant film front face where particle removal nature is low, and was excellent to it. this invention persons came to complete a header and this invention for these things.

[0029] That is, the summary of this invention consists in the washing approach which uses the penetrant remover and the penetrant remover concerned of the substrate for semiconductor devices characterized by containing the following components (A), (B), and (C) at least.

[0030] component (A): — the hydrocarbon group and polyoxyethylene radical which may have the substituent (except for a phenyl group) — having — the carbon number in a hydrocarbon group (m), and the oxyethylene in a polyoxyethylene radical — the ratio (m/n) of the base (n) — 1-1.5 — it is — a carbon number (m) — 9 or more and oxyethylene — the ethyleneoxide mold surfactant whose base (n) is seven or more.

(Component B): Water component (C): Alkali or an organic acid [0031]

[Embodiment of the Invention] Hereafter, this invention is explained to a detail. At least, the penetrant remover of this invention contains water as a specific surfactant and a component (B) as a component (A), and contains alkali or an organic acid as a component (C).

[0032] the hydrocarbon group and polyoxyethylene radical on which the surfactant used as a component (A) may have the substituent (except for a phenyl group) in this invention — having — the carbon number in a hydrocarbon group (m), and the oxyethylene in a polyoxyethylene radical — the ratio (m/n) of the base (n) — 1-1.5 — it is — a carbon number (m) — 9 or more and oxyethylene — the base (n) is the ethyleneoxide mold surfactant which is seven or more.

[0033] When the above-mentioned ratio (m/n) is less than one, it becomes inadequate corrosion controlling [of particle removal capacity or silicon] in liquid. Moreover, the load of the soluble fall to the water by the increase of oxyethylene chain length and waste fluid processing also increases. On the other hand, when exceeding 1.5, the emulsion of an O/W mold is formed in lye at the time of washing, and a surfactant serves as a fine oil droplet, it deposits and becomes cloudy, and problems, such as washing performance degradation and a residual of an oil droplet, are caused. Ratios (m/n) are 1-1.4 preferably.

[0034] When the above-mentioned carbon number (m) is less than nine, even if a ratio (m/n) is said optimal within the limits, particle removal nature falls. Moreover, when (m) is too large, since the soluble fall to water and the load of waste fluid processing also increase, it is not desirable. therefore, a carbon number (m) — desirable — 9-16 — it is 10-14 still more preferably. However, in case the hydrocarbon group which constitutes a component (A) has a hydrocarbon group as a substituent, it sets to m the total number of the carbon number in the hydrocarbon group used as a principal chain, and the hydrocarbon group which is a substituent.

[0035] Moreover, when the above-mentioned (n) is less than seven, even if a ratio (m/n) is said optimal within the limits, particle removal nature falls. When (n) is too large, the load of waste fluid processing becomes large, and it becomes easy to disassemble a surfactant in a penetrant remover. therefore, (n) — desirable — 7-16 — it is 7-14 still more preferably.

[0036] By using the above-mentioned ethyleneoxide mold surface active agent specified by this invention, both the wettability of a penetrant remover and the removal nature of particle become good. As the above-mentioned ethyleneoxide mold surface active agent, polyoxyethylene alkyl ether, polyoxyethylene fatty acid ester, polyoxyethylene alkylamine, a polyoxyethylene-alkyl-ether sulfate, etc. are mentioned, for example. The polyoxyethylene alkyl ether especially expressed with the following general formula (II) from viewpoints, such as the removal nature of particle contamination and reattachment prevention ability, is desirable.

[0037]

[Formula 2] R2O-(CH2CH2O)nH (II)

(However, R2 shows a hydroxyl group, the amino group, an alkoxy group, and the alkyl group that may be permuted with the halogen, the carbon number (m) contained in an alkyl group is nine or more, and (n) expresses seven or more numbers.)

[0038] As an example of the above-mentioned polyoxyethylene alkyl ether The polyoxyethylene (n= 8) nonyl ether, the polyoxyethylene (n= 9) DESHIRU ether, The polyoxyethylene (n= 11) undecyl ether, the polyoxyethylene (n= 10) lauryl ether, The polyoxyethylene (n= 11) lauryl ether, the polyoxyethylene (n= 10) tridecyl ether, The polyoxyethylene (n= 12) tridecyl ether, the polyoxyethylene (n= 11) tetradecyl ether, The polyoxyethylene (n= 13) tetradecyl ether, the polyoxyethylene (n= 12) pentadecyl ether, The polyoxyethylene (n= 14) pentadecyl ether, the polyoxyethylene (n= 12) cetyl ether, the polyoxyethylene (n= 15) cetyl ether, the polyoxyethylene (n= 18) oleyl ether, etc. are mentioned. In addition, the numeric value in the above-mentioned n expresses n in the aforementioned general formula (II).

[0039] In this invention, as long as it is within the limits of this invention, two or more ethyleneoxide mold surfactants with which (m) differs from (n) may be used together at a rate of arbitration. if the average of 9 or more and (n) fulfills [the average of (m/n) of all surfactants / the average of 1-1.5, and (m)] seven or more conditions in case two or more more sorts of surfactants are used together — the surfactant according to each individual — setting (m/n) — it may be over less than 1.0 and 1.5, or (m) may be less than nine and (n) may be less than seven.

[0040] The content of the component in a penetrant remover (A) is usually 0.001 - 0.05 % of the weight especially preferably 0.001 to 0.1% of the weight still more preferably 0.0003 to 0.5% of the weight preferably 0.0001 to 1% of the weight. When the concentration of a component (A) is too low, the particle decontamination engine performance is not enough, on the other hand, when the concentration of a component (A) is too high, it may become unsuitable for a washing process, and the load in the case of there being no change in the removal engine performance of particle contamination, and foaming becoming remarkable, and carrying out biodegradation processing of the waste fluid may increase.

[0041] In the gestalt usually sold, metal impurities of 1 - about 1000 ppm of numbers, such as Na, K, and Fe, may contain the component (A). In this case, a component (A) serves as a metal pollution source. Therefore, as for the surfactant used as a component (A), it is desirable to refine and use it. and the content of each metal impurity — usually — 10 ppm or less 1 ppm or less are preferably set to 0.1 ppm or less still more preferably. The method of dipping in ion exchange resin and, for example, making resin catch a

metal impurity as the purification approach, after dissolving a surfactant with water is suitable.

[0042] By using the component (A) refined as mentioned above, the penetrant remover by which the metal impurity content was reduced extremely can be obtained. Especially as a penetrant remover of this invention, it is desirable among the metal impurities in a penetrant remover that 5 or less ppb of contents of Na, Mg, aluminum, K, calcium, Fe, Cu, Pb, and Zn is 0.1 or less ppb also in 20 or less ppb at least.

[0043] In addition, in this invention, surfactants other than a component (A) may be used in the range which does not spoil the effectiveness of this invention. As surface active agents other than a component (A), any of a cation system surface active agent, an anion system surface active agent, and the Nonion system surface active agent are sufficient. using an anion system surfactant and the Nonion system surfactant especially — good — better ** — concrete — as for example, an anion system surfactant — ARUKI of carbon numbers 8-12 A RUBENZEN sulfonic acid and its salt, and alkyl methyl taurine acid of carbon numbers 8-12 and the salt, the alkyl-sulfuric-acid ester of carbon numbers 8-12, its salt, etc. mention — having — **. As an Nonion system surfactant, it is ****** which consists only of polyoxyalkylene. A sex agent etc. is mentioned.

[0044] In this invention, water is used as a component (B). quantity — the case where he wants to obtain a pure substrate front face — usually — deionized water — ultrapure water is used preferably. Moreover, the hydrogen water which made hydrogen gas dissolved in the electrolysis ion water obtained by the electrolysis of water and water can also be used.

[0045] In this invention, alkali or an organic acid is used as a component (C). That is, let the penetrant remover of this invention be an alkaline penetrant remover or an acid penetrant remover.

[0046] Although especially the class of alkali used by this invention is not limited, as typical alkali, ammonium hydroxide (aqueous ammonia solution) and organic alkali are mentioned. As organic alkali, amines, such as the 4th class ammonium of hydroxylation, an amine, and amino alcohol, are mentioned. What has a hydroxyl group, an alkoxy group, the alkyl group of the carbon numbers 1-4 which may be permuted with the halogen, or the hydroxyalkyl radical of carbon numbers 1-4 as the 4th class ammonium of hydroxylation is desirable, and even if all of these substituents are the same, they may differ.

[0047] As above alkyl groups, the low-grade alkyl group of the carbon numbers 1-4, such as a methyl group, an ethyl group, a propyl group, and butyl, is mentioned, and the low-grade hydroxyalkyl radical of the carbon numbers 1-4, such as a hydroxymethyl

group, a hydroxyethyl radical, a hydroxypropyl radical, and hydroxy butyl, is mentioned as a hydroxyalkyl radical.

[0048] As an example of the 4th class ammonium of hydroxylation of having the above-mentioned substituent, tetramethyl AMONIUMU hydroxide (TMAH), tetraethylammonium hydroxide, TORIMECHIRU (hydroxyethyl) ammonium hydroxide (common name: choline), triethyl (hydroxyethyl) ammonium hydroxide, etc. are mentioned. On the other hand, ethylenediamine, monoethanolamine, trimethano RUAMIN, etc. are mentioned as amines.

[0049] In above-mentioned alkali, the ammonium hydroxide from the reasons of that there are few cleaning effects and metal residuals, economical efficiency, the stability of a penetrant remover, etc., tetramethylammonium hydroxide (TMAH), and TORIMECHIRU (hydroxyethyl) ammonium hydroxide (common name: choline) are desirable. Such alkali may be used independently and two or more sorts may be used for it at a rate of arbitration.

[0050] Although what is necessary is just to choose the concentration of the alkali in a penetrant remover suitably, it is desirable that it is the concentration from which pH of a penetrant remover becomes nine or more alkalinity. The decontamination effectiveness which alkali concentration is too low, and is the purpose of this invention when pH is not high may not be acquired. On the other hand, since the danger that about [being economically disadvantageous] and a substrate front face will be damaged by etching, without acquiring the effectiveness by having raised pH when pH is too high increases, it is not desirable. therefore, pH of an alkaline penetrant remover — desirable — 9-13 — further — desirable — 10-12.5 — it is 10.5-12 especially preferably.

[0051] Although especially the class of organic acid used by this invention is not limited, an organic carboxylic acid or its organic sulfonic acid is desirable. As a typical thing of an organic carboxylic acid, formic acid, an acetic acid, a propionic acid, butanoic acid, an isobutyric acid, a valeric acid, ethyl methylacetic acid, trimethylacetic acid, oxalic acid, a succinic acid, a malonic acid, a citric acid, a tartaric acid, a malic acid, etc. are mentioned. In these, one sort chosen from the group of an acetic acid, a propionic acid, oxalic acid, a succinic acid, a malonic acid, a citric acid, a tartaric acid, and a malic acid or two sorts or more are desirable, and one sort chosen from the group of an acetic acid, oxalic acid, and a citric acid or two sorts or more are still more desirable. An acetic acid is the most desirable at the point that are used for the etchant ingredient of a semi-conductor substrate etc., and an object with few metal impurities can be cheap, can obtain by the high grade by distillation actuation, and generating of the fine particles by moisture evaporation does not take place, either.

[0052] As a typical thing of an organic sulfonic acid, methansulfonic acid, ethane sulfonic acid, n-propane sulfonic acid, i-propane sulfonic acid, n-butane sulfonic acid, a phenyl sulfonic acid, etc. are mentioned. In these, methansulfonic acid and/or ethane sulfonic acid are desirable, and especially methansulfonic acid is desirable. The above-mentioned organic acid may be used independently and two or more sorts may be used for it at a rate of arbitration.

[0053] Although what is necessary is just to choose the concentration of the organic acid in a penetrant remover suitably, it is desirable that it is the concentration from which pH of an acid penetrant remover is set to 1-5. The removal or the antisticking effectiveness of contamination which the concentration of an organic acid is too low, and are the purpose of this invention when pH is not sufficiently low may not be acquired. On the other hand, when concentration is too high, it is economically disadvantageous, without acquiring the effectiveness by having reduced pH, and since it can also become the cause of the corrosion on about [that it is] and the front face of a substrate, it is not desirable. pH of an acid penetrant remover is 2-3 preferably.

[0054] In the penetrant remover of this invention, since the front face which reduced further the metal contamination on the front face of a substrate and which was extremely defecated by altitude will be obtained if a complexing agent is made to contain, it is desirable. As a complexing agent, the thing of well-known arbitration can be used conventionally. What is shown by the following (1) - (4) is mentioned that what is necessary is to judge the class of complexing agent synthetically and just to choose it from the contamination level on the front face of a substrate, a metaled class, the cleanliness level required of a substrate front face, complexing agent cost, chemical stability, etc.

[0055] The compound which has the nitrogen, carboxyl group, and/or phosphonic acid radical which are a donor atom : (1) For example Amino acid, such as a glycine; Imino 2 acetic acid, nitrilotriacetic acid, ethylenediaminetetraacetic acid [EDTA], A transformer -1, 2-diamino cyclohexane 4 acetic acid [CyDTA], Nitrogen-containing carboxylic acids, such as diethylenetriamine pentaacetic acid [DTPA] and triethylenetetramine 6 acetic acid [TTHA]; Ethylenediamine tetrakis (methylene phosphonic acid) [EDTPO], Nitrogen-containing phosphonic acid, such as NITORIRO tris (methylene phosphonic acid) [NTPO] and a propylenediamine tetrapod (methylene phosphonic acid) [PDTMP], is mentioned.

[0056] (2) Phenols, such as compound:, for example, a catechol, which has the OH radical and/or two O-radicals or more which were coupled directly with the carbon atom which has an aromatic hydrocarbon ring and constitutes an aromatic hydrocarbon ring,

resorcinol, and tiron, the derivative of those, etc. are mentioned.

[0057] (3) Compound having the above (1) and the structure of (2) : [0058] An ethylenediamine JIORUTO hydroxyphenyl acetic acid [EDDHA] and its derivative : (3-1) For example An ethylenediamine JIORUTO hydroxyphenyl acetic acid [EDDHA], Ethylenediamine-N, N'-screw [(2-hydroxy-5-methylphenyl) acetic-acid] [EDDHMA], Ethylenediamine-N, N'-screw [(2-hydroxy-5-KURORU phenyl) acetic-acid] [EDDHCA], an ethylenediamine-N and N'-screw — aromatic series nitrogen-containing carboxylic-acids; ethylenediamine-N, such as [(2-hydroxy-5-sulfophenyl) an acetic acid [EDDHSA]], and N' - screw [(2-hydroxy-5-methylphenyl) phosphonic acid] — Aromatic series nitrogen-containing phosphonic acid, such as an ethylenediamine-N and N'-screw [(2-hydroxy-5-phospho phenyl) phosphonic acid], is mentioned.

[0059] N, N'-bis(2-hydroxybenzyl) ethylenediamine-N, N'-2 acetic-acid [HBED], and its derivative : (3-2) For example N, N'-bis(2-hydroxybenzyl) ethylenediamine-N, N'-2 acetic-acid [HBED], N, N'-bis(2-hydroxy-5-methylbenzyl) ethylenediamine-N, N'-2 acetic-acid [HMBED], N, N'-bis(2-hydroxy-5-KURORU benzyl) ethylenediamine-N, N'-2 acetic acid, etc. are mentioned.

[0060] (4) In addition, hydrogen halides, such as carboxylic-acids; hydrofluoric acids, such as amines; formic acids, such as :, for example, ethylenediamine, an eight quinolinol, and o-phenanthrolin, an acetic acid, oxalic acid, and a tartaric acid, a hydrochloric acid, a hydrogen bromide, and hydrogen iodide, those salts; oxo acid, such as a phosphoric acid and condensed phosphoric acid, those salts, etc. are mentioned.

[0061] The thing of the gestalt of an acid may be used for the above-mentioned complexing agent, and the thing of the gestalt of salts, such as ammonium salt, may be used for it.

[0062] the inside of the complexing agent mentioned above — nitrogen-containing phosphonic acid; ethylenediamine JIORUTO hydroxyphenyl acetic acids [EDDHA], such as nitrogen-containing carboxylic-acids; ethylenediamine tetrakis (methylene phosphonic acid) [EDTPO], such as ethylenediaminetetraacetic acid [EDTA] and diethylenetriamine pentaacetic acid [DTPA], and a propylenediamine tetrapod (methylene phosphonic acid) [PDTMP], and derivative;N of those from the reasons of a cleaning effect, chemical stability, etc., and N' - bis(2-hydroxybenzyl) ethylenediamine-N and N' -2 acetic acid [HBED] is desirable.

[0063] inside — **** — a cleaning effect — a viewpoint — from — Ellen — diamine — JIORUTO — hydroxyphenyl — an acetic acid — [— EDDHA —] — ethylenediamine - N — N — ' - a screw — [(2-hydroxy-5-methylphenyl) — an acetic acid —] — [— EDDHMA —] — diethylenetriamine pentaacetic acid — [— DTPA —] — ethylenediaminetetraacetic acid

— [— EDTA —] — propylenediamine — a tetrapod (methylene phosphonic acid) — [— PDTMP —] — being desirable . The above-mentioned complexing agent may be used independently and two or more sorts may be used for it at a rate of arbitration.

[0064] Although what is necessary is just to choose the concentration of the complexing agent in a penetrant remover as arbitration with the class of contamination metal impurity, an amount, and the cleanliness level required of a substrate front face, it is 1-10000 ppm usually 10-200 ppm still more preferably 5-1000 ppm preferably. When the concentration of a complexing agent is too low, the decontamination or the antisticking effectiveness by the complexing agent are not acquired, but a complexing agent adheres to about [being economically disadvantageous] and a substrate front face, without acquiring the effectiveness of balancing the increment in concentration, when too high, and the danger of remaining after surface treatment increases.

[0065] In addition, since the complexing agent contains metal impurities, such as FeAl of 1 - about 1000 ppm of numbers, and Zn, in the reagent usually sold, it can consider the case where the complexing agent used by this invention serves as a metal pollution source. Although these metals form a complexing agent and a stable complex and exist in early stages, if a complexing agent decomposes while carrying out long duration use as a surface penetrant remover, they will separate and will adhere to a substrate front face. Therefore, as for the complexing agent used by this invention, it is desirable to use it, refining beforehand. and the content of each metal impurity contained — usually — 5 ppm or less 1 ppm or less are preferably set to 0.1 ppm or less still more preferably. As the purification approach, after dissolving a complexing agent in acidity or an alkaline solution for example, filtration separation is carried out and an insoluble impurity is removed, and it neutralizes again, a crystal is deposited, and the method of separating the crystal concerned with liquid is suitable.

[0066] Moreover, the penetrant remover of this invention may contain other components at a rate of arbitration in the range which does not spoil the engine performance. as other components — a sulfur-containing organic compound (2-mercapto thiazoline —) 2-mercapto imidazoline, 2-mercaptoethanol, the thioglycerol, etc., a nitrogen-containing organic compound (benzotriazol and alkyl benzotriazol —) A tetra-SOL, 3-aminotriazole, N3 (R is the alkyl group of carbon numbers 1-4) (R), N(ROH) 3 (R is the alkyl group of carbon numbers 1-4), urea, thiourea, etc., A water-soluble polymer (a polyethylene glycol, polyvinyl alcohol, etc.), Anticorrosives, such as an alkyl alcoholic system compound (ROH (R is the alkyl group of carbon numbers 1-4)), The etching accelerator which can expect the removal effectiveness, such as a polymer which adhered firmly, is mentioned after dry etching, such as

dissolved gas, such as reducing agents, such as acids, such as a sulfuric acid and a hydrochloric acid, and a hydrazine, hydrogen, an argon, and nitrogen, fluoric acid, ammonium fluoride, and BHF.

[0067] And oxidizers, such as a hydrogen peroxide, ozone, and oxygen, are also mentioned as other components which the penetrant remover of this invention is made to contain. In the washing process of the substrate for semiconductor devices, in case a silicon (BEASHIRIKON) substrate front face without an oxide film is washed, since the surface dry area by etching to a substrate front face can be stopped by combination of an oxidizing agent, it is desirable. When making the alkaline penetrant remover of this invention contain a hydrogen peroxide, hydrogen-peroxide concentration in a penetrant remover is usually preferably made into 0.1 - 1 % of the weight 0.01 to 5% of the weight.

[0068] By the way, wiring of a semiconductor device and the device component electrode which consist of a metallic material which reacts with a hydrogen peroxide and dissolves may be exposed to the front face of the substrate to wash. As such a metallic material, transition metals or transition-metals compounds, such as Cu and W, are mentioned, for example. Under the present circumstances, as for the penetrant remover used for washing, it is desirable not to contain a hydrogen peroxide substantially. The penetrant remover of this invention shows sufficient washing engine performance, without having a bad influence on such a metallic material, even if it does not contain a hydrogen peroxide substantially unlike the conventional APM penetrant remover.

[0069] In addition, in the penetrant remover of this invention, it means not producing bad influences, such as corrosion, deterioration, etc. by the hydrogen peroxide, to wiring materials and electrode materials, such as the ingredient on the substrate washed saying "a hydrogen peroxide is not contained substantially", for example, Cu, and W, and the low dielectric constant film. That is, when these ingredients consider as a semiconductor device, it means fully functioning as wiring, an electrode, etc. For that purpose, it is so desirable that the content is stopped few even if a hydrogen peroxide is not contained in the penetrant remover of this invention, and it makes and being contained. the content — for example, 1 ppm 10 ppm or less are preferably set to 10 or less ppb still more preferably.

[0070] The penetrant remover of this invention is used for washing on front faces of a substrate, such as the semi-conductor with which metal contamination and particle contamination pose a problem, glass, a metal, ceramics, resin, the magnetic substance, and a superconductor. especially — quantity — it is used suitable for washing on the

front face for semiconductor devices of a substrate in the process which manufactures the substrates for semiconductor devices a semiconductor device, for display devices, etc. with which a pure substrate front face is demanded. Wiring, an electrode, etc. may exist in the front face of these substrates. As an ingredient of wiring or an electrode, metals, such as insulating material;W, such as semiconductor material;SiO(s)2, such as Si, germanium, and GaAs, silicon nitride, glass, a low dielectric constant ingredient, an aluminum oxide, transition-metals oxide (titanium oxide, tantalum oxide, an oxidization hafnium, zirconium dioxide, etc.), TiO(Ba, Sr) 3 (BST), polyimide, and organic thermosetting resin, and Cu, aluminum, or these alloys, silicide, a nitride, etc. are mentioned. A low dielectric constant ingredient is the generic name of the ingredient whose specific inductive capacity is 3.5 or less. Incidentally, the specific inductive capacity of SiO2 is 3.8-3.9.

[0071] Especially the penetrant remover of this invention is used suitable for washing of the substrate for semiconductor devices which has transition metals or a transition-metals compound on a front face. As transition metals, W, Cu, Ti, Cr, Co, Zr, Hf, Mo, Ru, Au, Pt, Ag, etc. are mentioned, and the CHITSU ghost of these transition metals, an oxide, silicide, etc. are mentioned as a transition-metals compound. In these, W and/or Cu are desirable.

[0072] As a process which washes the substrate which has a tungsten, washing on the front face of a substrate which has a gate electrode, silicon, etc. at the time of using a tungsten as a gate electrode material is mentioned to a front face. Specifically, the washing process after forming the tungsten film in a semiconductor device, the washing process after carrying out dry etching of the tungsten film especially, and the washing process after carrying out an ion implantation to a silicon outcrop after that are mentioned.

[0073] If the penetrant remover of this invention is used, even if it performs neither ultrasonic irradiation nor a brush scrub, a particle metallurgy group is removable. Therefore, the penetrant remover of this invention is suitable for washing of a gate electrode and a substrate front face when a possibility of breaking if ultrasonic cleaning and a brush scrub are performed forms a very detailed (for example, the width of face of a gate electrode is about 0.15 micrometers) large gate electrode with a tungsten.

[0074] As a process which washes the substrate which has Cu, washing on the front face of a substrate which has Cu wiring, an interlayer insulation film, etc. at the time of using Cu as a wiring material is mentioned to a front face. Specifically, the washing process after forming Cu film in a semiconductor device especially the washing process after performing CMP (Chemical Mechanical Polishing) to Cu film, and the washing process

after opening a hole in the interlayer insulation film on wiring by dry etching are mentioned.

[0075] Moreover, the penetrant remover of this invention is used suitable also for washing of the substrate for semiconductor devices which has a low dielectric constant ingredient used as an interlayer insulation film ingredient on a front face. As a low dielectric constant ingredient, it is roughly divided into three with an organic polymer ingredient, an inorganic polymer (siloxane system) ingredient, and a porosity (porous) ingredient. As an organic polymer ingredient, Polyimide, BCB (Benzocyclobutene), Flare (Honeywell), SiLK (Dow Chemical), etc. are mentioned, and FSG (Fluorinated silicate glass), BLACK DIAMOND (Applied Materials), Aurora (Japan ASM), etc. are mentioned as an inorganic polymer ingredient.

[0076] The penetrant remover of this invention is used suitable for the surface washing of the substrate for semiconductor devices irrespective of the existence of the electrode in a substrate front face, or a wiring material as mentioned above. Also in it, the penetrant remover of this invention is used suitable for washing of the substrate for semiconductor devices which the contact angle of the water in a substrate front face shows hydrophobicity 60 degrees or more.

[0077] The preparation approach of the penetrant remover of this invention should just be conventionally based on a well-known approach. Any 2 components or three components or more in the constituent (for example, accepting a surfactant, ammonium hydroxide, water, and the need other components, such as a complexing agent) of a penetrant remover may be blended beforehand, the remaining components may be mixed after that, and all may be mixed at once.

[0078] As mentioned above, also with the substrate for semiconductor devices which has a metallic material with low resistance in a front face to drug solutions, such as a future exotic material, i.e., a hydrogen peroxide etc., since the substrate penetrant remover for semiconductor devices of this invention does not corrode these exotic materials substantially, it turns into an usable penetrant remover which does the outstanding cleaning effect so at both a last process and a back process.

[0079] That is, other summaries of this invention consist in the substrate penetrant remover for semiconductor devices which is characterized by filling the following conditions (a), (b), and (c) and which has a semiconductor device electrode or metal wiring on a front face at least.

[0080] (a) Don't corrode a semiconductor device electrode and metal wiring substantially.

(b) When the amount of contamination metals washes the substrate which are

1000-5000 (x1010 atoms/cm2), the amount of contamination metals after washing is below ten (x1010 atoms/cm2).

(c) [when the approximate circle configuration substrate front face of the radius r which has particle with a particle size of 0.1 micrometers or more 8000-100000 (an individual / 0.03m2) is washed between t (minute)] The particle number within the periphery on the substrate front face which makes a substrate and a core the same is 800/t or less piece within the periphery of periphery radius 0.6r after washing within 200/t or less piece or the periphery of periphery radius 0.9r in the case of t=0.5-1.

[0081] In addition, a convention of the above-mentioned (b) and (c) is not what specified the property of the penetrant remover of this invention and specified the washing conditions for which the penetrant remover of this invention is used. Moreover, in the penetrant remover of this invention, semiconductor device electrode metallurgy group wiring on the substrate washed saying "a semiconductor device electrode and metal wiring are not corroded substantially", and when it does not produce bad influences, such as corrosion and deterioration, and these ingredients specifically consider as a semiconductor device to electrode materials and wiring materials, such as W and Cu, it means fully functioning as an electrode, wiring, etc.

[0082] In the penetrant remover of above-mentioned this invention, filling conditions (b) and (c) shows that it is possible to fully remove metal contamination, particle contamination, and any contamination.

[0083] In case the candidate for washing is the front face of an approximate circle tabular substrate, i.e., an approximate circle configuration substrate front face, even if conditions (c) are short-time washing, they do not call at the location on the front face of a substrate, but mean that a substrate front face can be defecated to altitude. that is, the approximate circle configuration substrate front face of the radius r which has particle with a particle size of 0.1 micrometers or more 8000-100000 (an individual / 0.03m2) — a part for washing time amount t:0.5 - 1[—] — ******, after washing Within the periphery of periphery radius 0.6r on the substrate front face made the same which is the inner circumference section comparatively, a substrate and a core Particle is made into 800/t or less piece also into the periphery of periphery radius 0.9r which removes the particle which remains to 200/t or less piece, and contains even the periphery section comparatively, and it means that a substrate front face can be defecated to altitude.

[0084] moreover, it can set to the substrate penetrant remover for semiconductor devices of this invention mentioned above — "— the case where it washes — setting — " — it is shown by the washing approach which is mentioned later that it is the case where a penetrant remover washes the substrate for semiconductor devices. The washing

approach will not usually be limited, especially if it is the approach which may be adopted at the time of washing of the substrate for semiconductor devices. Especially, the contact approach to the substrate of a penetrant remover makes a penetrant remover on a substrate the spin type which carries out high-speed rotation of the substrate with a sink, and since the result by which considering as the range of room temperature -90 degree C was stabilized is obtained, whenever [solution temperature / of a penetrant remover] is desirable.

[0085] Furthermore, since the washing result of having been stabilized more by adopting mechanical cleaning, such as scrub washing which used the washing approach by physical force, for example, a washing brush, ultrasonic cleaning which irradiates a supersonic wave with a frequency of 0.5MHz or more at a substrate, the washing approach which uses these together, etc. is obtained in the case of washing, it is desirable.

[0086] The washing approach of this invention is performed by the approach of contacting a penetrant remover to a substrate directly. The DIP type which a penetrant remover is filled [type] to a cleaning tank and makes a substrate immersed in the contact approach to the substrate of a penetrant remover, the spin type which carries out high-speed rotation of the substrate for a penetrant remover with a sink on a substrate from a nozzle, the spray ceremony which sprays and washes liquid at a substrate are held. There are a batch type washing station which washes to coincidence two or more substrates held in the cassette as equipment for performing such washing, a single-wafer-processing washing station which equips an electrode holder with one substrate and washes it.

[0087] In the case of a batch type washing station, in the case of a single-wafer-processing washing station, washing time amount is usually 5 minutes from 5 seconds preferably from 1 second from 30 seconds for 15 minutes for 1 to 15 minutes for 30 minutes. When too long [when washing time amount is too short, a cleaning effect is not enough, and], the improvement in a cleaning effect is small and causes the fall of a throughput. Although the penetrant remover of this invention is applicable to any above-mentioned approach, it is preferably used for washing of a spin type or a spray type from the point which can perform more efficient decontamination for a short time. And if compaction of ** and washing time amount and reduction of the amount of the penetrant remover used apply to the single-wafer-processing washing station which poses a problem, since these problems are solved, it will be desirable.

[0088] Although temperature of a penetrant remover is usually made into a room temperature, it is the purpose which raises a cleaning effect and it is desirable to warm

at about 40-70 degrees C. Furthermore, when washing the substrate which silicon has exposed to a front face, in order that organic substance contamination may tend to remain on a silicon front face, it is desirable to offer and carry out the pyrolysis of the substrate to heating down stream processing with a temperature of 300 degrees C or more, or to carry out the oxidative degradation place of the organic substance by ozone water treatment.

[0089] Moreover, as for the washing approach of this invention, it is desirable to make it use together with mechanical cleaning, such as scrub washing which used the washing approach by physical force, for example, a washing brush, or ultrasonic cleaning. If ultrasonic irradiation or a brush scrub is especially used together, since the removal nature of particle contamination improves further and leads also to compaction of washing time amount, it will be desirable. It is desirable to wash by washing after CMP especially using the brush made of resin.

[0090] Although the quality of the material of the brush made of resin can be chosen as arbitration, it is desirable to use PVA (polyvinyl alcohol), for example. Moreover, if a supersonic wave with a frequency of 0.5MHz or more is irradiated at a substrate, since the removal nature of particle improves remarkably according to a synergism with a surface active agent, it will be desirable. Furthermore, washing by the electrolysis ion water obtained by the electrolysis of water or the hydrogen water which made hydrogen gas dissolved in water may be combined before the washing approach of this invention, and/or with the back.

EXAMPLE

[Example] Next, it is not limited by the following examples unless this invention exceeds the summary according to an example, although this invention is explained concretely.

[0092] The 8 inch silicon substrate (disc-like substrate whose radius r is 4 inches) examples 1 and 2 and the example 1 of a comparison - with 3 (detergency evaluation of the particle contamination by scrub type washing) low dielectric constant film (SiOC: carbon content SiO2) was immersed in the SiO2 slurry solution for 10 minutes. The substrate after immersion was rinsed for 1 minute with ultrapure water, and spin desiccation was carried out with the multi-spinner (Made in Khai Joe "KSSP-201"). Then, it checked that measured the particulate number adhering to a substrate front face, and SiO2 particle 0.2 micrometers or more had adhered more than fixed quantity (however, an upper limit 100000 pieces) with laser surface-analysis equipment ("LS-5000" by Hitachi Electronics Engineering).

[0093] The penetrant remover shown in Table 1 was used, with the above-mentioned multi-spinner, brush scrub washing of the above-mentioned SiO2 particle adhesion substrate was carried out with the brush made from PVA, and particle was removed. Washing by the penetrant remover was performed for 1 minute at the room temperature. Then, after ultrapure water washed the substrate for 1 minute, spin desiccation was carried out and the washed substrate was obtained. A result is shown in Table 1.

[0094]

[Table 1]

[0095] examples 3-6 and the examples 4-8 (detergency evaluation of the particle contamination by scrub type washing) of a comparison — the SiO2 particle adhesion substrate was first created like the example 1. Subsequently, the penetrant remover shown in Table 2 was used, except having set washing time amount as for 0.5 minutes, the SiO2 particle adhesion substrate was washed like the example 1, and the washed substrate was obtained. A result is shown in Table 2.

[0096] Wettability evaluation in Table 2 was performed by the following approach. Namely, it soaks at right angles to each penetrant remover given [the piece of a test (2cm angle) with the low dielectric constant film (SiOC: carbon content SiO2)] in Table 2. The piece of a test was perpendicularly pulled out after 0.5 minutes, and the rate of area that the penetrant remover to the whole surface product of the piece of a test was attached estimated. The valuation basis was made into more than O:80%, less than

[more than **:50%80%], and less than [x:50%].

[0097]

[Table 2]

[0098] After carrying out surface treatment of the 8 inch silicon substrate (disc-like substrate whose radius r is 4 inches) an example 7 - with 10 (detergency evaluation of the particle contamination by scrub type washing) low dielectric constant film (SiOC: carbon content SiO2) for 1 minute by fluoric acid 0.5% of the weight, it was immersed in the SiO2 slurry solution for 10 minutes. The substrate after immersion was rinsed for 1 minute with ultrapure water, and spin desiccation was carried out with the multi-spinner (Made in Khai Joe "KSSP-201"). Then, the particulate number which adhered to the substrate front face with laser surface-analysis equipment ("LS-6600" by Hitachi Electronics Engineering) was measured, and it checked that SiO2 particle 0.11 micrometers or more had adhered more than fixed quantity (however, an upper limit 100000 pieces).

[0099] The penetrant remover shown in Table 3 was used, with the above-mentioned multi-spinner, brush scrub washing of the above-mentioned SiO2 particle adhesion

substrate was carried out with the brush made from PVA, and particle was removed. Washing by the penetrant remover was performed for 0.5 minutes at the room temperature. Then, after ultrapure water washed the substrate for 1 minute, spin desiccation was carried out and the washed substrate was obtained. A result is shown in Table 3.

[0100]

[Table 3]

[0101] examples 11 and 12 and the example 9 (detergency evaluation of the particle contamination by scrub type washing) of a comparison — the SiO2 particle adhesion substrate was first created like the example 1. Subsequently, the penetrant remover shown in Table 4 was used, except having set washing time amount as for 0.5 minutes, the SiO2 particle adhesion substrate was washed like the example 1, and the washed substrate was obtained. A result is shown in Table 4.

[0102]

[Table 4]

[0103] The 4 inch silicon substrate (disc-like substrate whose radius r is 2 inches) to which the thermal oxidation film with a thickness of about 100nm was attached to the example 13 and the example of comparison 10 substrate front face was exposed into atmospheric air for 3 hours, and the suspended matter in mind was made to adhere. As a result of measuring with substrate surface-analysis equipment ("LS-5000" by Hitachi Electronics Engineering), particle with a particle size of 0.2 micrometers or more was carrying out 10,000 or more (however, upper limit 100000 pieces) piece adhesion at the base. the stream by the pure water during 10 minutes after carrying out immersion processing of this substrate for 10 minutes each at each penetrant remover given in Table 3 by which temperature control was carried out to 50 degrees C — it washed and dried with the spin dryer. The measurement result of the number of particle which remains on the substrate after washing processing is shown in Table 5.

[0104] In example of comparison 11 example 13, except having used the solution (APM penetrant remover) which mixed an ammonium hydroxide water solution, 50-% of the weight hydrogen peroxide solution, and ultrapure water by the capacity factor 1:4:20 29% of the weight, and was prepared as a penetrant remover, it carried out like the example 13 and evaluated. A result is shown in Table 5.

[0105] Although the penetrant remover of the example 11 of a comparison has comparatively few adhesion particle numbers after washing, since a hydrogen peroxide is included in a penetrant remover, it cannot perform application to a future exotic material, but becomes unusable in the future.

[0106]

[Table 5]

[0107] The substrate from which immersion processing of the 4 inch silicon substrate (disc-like substrate whose radius r is 2 inches) to which an example 14 and the example 12 of a comparison - 14 natural oxidation film were attached was carried out for 5 minutes 0.5% of the weight at HF water solution, and the scaling film was removed was obtained. the stream carry out immersion processing of this for 10 minutes at each penetrant remover given in Table 4 by which Silicon(IV) Nitride particle (product made from Johnson Matthey "Stk#12145") 0.02 g/L was added, and temperature control was carried out to 50 degrees C, and according to after and the pure water during 5 minutes — it washed and dried with the spin dryer. With substrate surface-analysis equipment ("LS-5000" by Hitachi Electronics Engineering), the number of particle with a particle size of 0.2 micrometers or more which remains on the substrate after washing processing was measured. A result is shown in Table 6.

[0108]

[Table 6]

[0109] The 4 inch silicon substrate (disc-like substrate whose radius r is 2 inches) which removed the surface natural oxidation film was prepared for the example 15 and the 15,160.5 % of the weight HF water solution of examples of a comparison by carrying out immersion processing for 5 minutes. the stream by the pure water during 5 minutes after carrying out predetermined time immersion processing of this at a penetrant remover given in each table 5 by which temperature control was carried out — it washed and dried with the spin dryer. after substrate desiccation — immediately — an atomic force microscope (Nano ScopeIIIa made from Digital Instruments) — the Z-axis on the front face of a substrate — Rms (nm) which is the standard deviation of a variation rate was measured. A result is shown in Table 7.

[0110] It is a deed about evaluation according to viewing about the surface dry area of the above-mentioned substrate. The following result was obtained. That is, in the case of the examples 15 and 16 of a comparison, a surface dry area like the interference fringe covering countless crater-like irregularity with a diameter of about about 1-10mm and the whole substrate front face was observed on the substrate front face, but in the case of the example 15, it was not observed.

[0111]

[Table 7]

[0112] The piece of a test of the polycrystal polish recon of about 100nm of thickness which removed the scaling film was prepared for examples 16-19 and the 17 - 190.5 % of the weight HF water solution of examples of a comparison by carrying out immersion processing for 5 minutes. the stream by the pure water during 5 minutes after carrying out immersion processing of this piece of a test for 10 minutes at each penetrant remover given in Table 6 by which temperature control was carried out to 50 degrees C — it washed and dried by the nitrogen blow. The thickness of polycrystal polish recon was measured with the optical interference type thickness measurement vessel (the "nano spec. L-6100" by the nano metrics company). The etching rate was computed from the thickness measurement before and behind washing processing. A result is shown in Table 8.

[0113]

[Table 8]

[0114] The piece of a test of the tungsten of about 100nm of thickness which removed the scaling film was prepared for the example 20 and the 10.3 % of the weight aqueous ammonia solution of examples of reference by carrying out immersion processing for 5 minutes. the stream by the pure water during 5 minutes after carrying out immersion processing of this piece of a test for 10 minutes at each penetrant remover given in Table 9 by which temperature control was carried out to 40 degrees C — it washed and dried by the nitrogen blow. The thickness of a tungsten used total reflection fluorescence X rays (product made from Jeol "RIX-3000"), and drew them by the conversion from reflectivity. The etching rate was computed from the thickness measurement before and behind washing processing. A result is shown in Table 9.

[0115] Here, it turns out that an example 20 is compared with the example 1 of reference, and the penetrant remover of this invention controls the etching rate on the front face of a substrate to a mere alkali water solution, and it excels as a substrate penetrant remover for semiconductor devices the clear passage.

[0116] In example of comparison 20 example 20, except having used the same APM penetrant remover as the example 11 of a comparison as a penetrant remover, it carried out like the example 20 and evaluated. A result is shown in Table 9.

[0117]

[Table 9]

[0118] The example 21 and the 214 inches silicon substrate (disc-like substrate whose radius r is 2 inches) of examples of a comparison were immersed in the APM penetrant remover containing a metal ion (Fe, Cu). This APM penetrant remover mixed aqueous ammonia, 31-% of the weight hydrogen peroxide solution, and water by the capacity factor 1:1:5 29% of the weight, and it added and prepared the metal ion content water solution so that a metal content might serve as Fe (20ppb) and Cu (1 ppm) at this. The silicon substrate after immersion was rinsed for 10 minutes with ultrapure water, it dried by nitrogen blow, and the silicon substrate polluted with the metal was obtained.

[0119] The polluted silicon substrate and the silicon substrate after washing performed analysis of the contamination metal on this silicon substrate (Fe, Cu) by the following approach. That is, it collects by processing a substrate in the water solution which contains 0.1 % of the weight of fluoric acid, and 1 % of the weight of hydrogen peroxides for the metal in a substrate front face, the amount of metals is measured with an inductively-coupled-plasma-source-mass-spectrometry plan (ICP-MS), and it converts into the metal concentration (atoms/cm2) on the front face of a substrate.

[0120] The penetrant remover which shows washing of the above-mentioned silicon substrate polluted with the metal in Table 10 was used, and it considered as penetrant remover temperature [of 60 degrees C], and washing time amount 10 minutes, and carried out by the DIP type cleaning method. The analysis result of the polluted silicon substrate and the residual metal (Fe, Cu) of a washed silicon substrate surface are shown in Table 10.

[0121]

[Table 10]

[0122] It is clear from the above result the penetrant remover's of this invention to excel in the removal nature of the particle (particle) adhering to the low dielectric constant film which is hydrophobicity. Moreover, it compares with the conventional washing approach by the ammonium hydroxide solution or the APM solution, and it turns out that it has the more excellent removal nature also to the particle affix of the suspended matter origin in mind.

[0123] Similarly, even if a particle (particle) etc. mixes in a system, it becomes possible by removing by the washing approach of this invention to control adhesion in a substrate. Furthermore, it becomes as compared with the conventional washing approach, it is possible to control very small the roughness on the front face of silicon (front face that) also in an alkaline penetrant remover, and possible for there to be almost no side effects, such as polish recon and a processing dimensional change by etching to a tungsten, and to be compatible in detergency, roughness control, and low etching nature.

[0124] And even if the penetrant remover of this invention is a substrate for semiconductor devices which has an ingredient with low resistance in a front face to drug solutions, such as a hydrogen peroxide, it is clear to both a last process and a back process that it is the usable penetrant remover which does the outstanding cleaning effect so.

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(54)【発明の名称】半導体デバイス用基板の洗浄液および洗浄方法

(57)【要約】
【課題】半導体デバイス用基板に於いて、基板表面を腐食することなく、基板表面に付着した微粒子や有機汚染を洗浄により除去し、基板表面を高度に清浄化する基板表面の洗浄液および洗浄方法を提供する。
【解決手段】少なくとも、以下の成分（A）、（B）及び（C）を含有することを特徴とする半導体デバイス用基板の洗浄液および当該洗浄液を使用した洗浄方法。
成分（A）：置換基（フェニル基を除く）を有していてもよい炭化水素基とポリオキシエチレン基とを有し、炭化水素基中の炭素数（m）とポリオキシエチレン基中のオキシエチレン基数（n）の比率（m／n）が１～１．５であり、炭素数（m）が９以上、オキシエチレン基数（n）が７以上であるエチレンオキサイド型界面活性剤。
成分（B）：水
成分（C）：アルカリ又は有機酸

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【特許請求の範囲】

【請求項１】　少なくとも、以下の成分（Ａ）、（Ｂ）及び（Ｃ）を含有することを特徴とする半導体デバイス用基板の洗浄液。

成分（Ａ）：置換基（フェニル基を除く）を有していてもよい炭化水素基とポリオキシエチレン基とを有し、炭化水素基中の炭素数（ｍ）とポリオキシエチレン基中のオキシエチレン基数（ｎ）の比率（ｍ／ｎ）が１～１．５であり、炭素数（ｍ）が９以上、オキシエチレン基数（ｎ）が７以上であるエチレンオキサイド型界面活性剤。

成分（Ｂ）：水

成分（Ｃ）：アルカリ又は有機酸

【請求項２】　成分（Ａ）における炭素数（ｍ）が９～１６である請求項１に記載の洗浄液。

【請求項３】　成分（Ｃ）としてアルカリを含有し、ｐＨが９以上である請求項１又は２に記載の洗浄液。

【請求項４】　成分（Ｃ）が以下の一般式（Ｉ）で表されるアルカリ化合物である請求項３に記載の洗浄液。

【化１】　$(R^1)_4 N^+ OH^-$　　（Ｉ）

（但し、R^1 は水素原子、又は水酸基、アルコキシ基、ハロゲンにて置換されていてもよいアルキル基を示し、R^1 は全て同一でも異なっていてもよい。）

【請求項５】　成分（Ｃ）が水酸化アンモニウム若しくは炭素数１～４のアルキル基および／またはヒドロキシアルキル基を有する水酸化第４級アンモニウムである請求項４に記載の洗浄液。

【請求項６】　成分（Ｃ）として有機酸を含有し、ｐＨが１～５である請求項１又は２に記載の洗浄液。

【請求項７】　成分（Ｃ）が有機カルボン酸および／または有機スルホン酸である請求項６に記載の洗浄液。

【請求項８】　有機カルボン酸が、酢酸、プロピオン酸、蔭酸、コハク酸、マロン酸、クエン酸、酒石酸、リンゴ酸から成る群より選ばれる少なくとも１種である請求項７に記載の洗浄液。

【請求項９】　有機スルホン酸が、メタンスルホン酸、エタンスルホン酸、ｎ－プロパンスルホン酸、ｉ－プロパンスルホン酸、ｎ－ブタンスルホン酸から成る群より選ばれる少なくとも１種である請求項７に記載の洗浄液。

【請求項１０】　成分（Ａ）の含有量が０．０００１～１重量％である請求項１～９の何れかに記載の洗浄液。

【請求項１１】成分（Ａ）がポリオキシエチレンアルキルエーテル類である請求項１～１０の何れかに記載の洗浄液。

【請求項１２】更に錯化剤を含有する請求項１～１１の何れかに記載の洗浄液。

【請求項１３】実質的に過酸化水素を含有しない請求項１～１２の何れかに記載の洗浄液。

【請求項１４】請求項１～１３の何れかに記載の洗浄液

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を使用することを特徴とする半導体デバイス用基板の洗浄方法。

【請求項１５】周波数０．５メガヘルツ以上の超音波を照射しながら基板を洗浄する請求項１４に記載の洗浄方法。

【請求項１６】化学的機械研磨した後の半導体デバイス用基板をブラシ洗浄する請求項１４又は１５に記載の洗浄方法。

【請求項１７】洗浄液を４０～７０℃の温度に加温して使用する請求項１４～１６の何れかに記載の洗浄方法。

【請求項１８】洗浄液で洗浄した後、更に温度３００℃以上の加熱処理か又はオゾン水処理を行う請求項１４に記載の洗浄方法。

【請求項１９】表面に水の接触角が６０°以上の絶縁膜を有する半導体デバイス用基板に適用する請求項１４に記載の洗浄方法。

【請求項２０】表面にシリコン、遷移金属または遷移金属化合物を有する半導体デバイス用基板に適用する請求項１４に記載の洗浄方法。

【請求項２１】以下の条件（ａ）、（ｂ）及び（ｃ）を満たすことを特徴とする、少なくとも半導体素子電極または金属配線を表面に有する、半導体デバイス用基板洗浄液。

（ａ）実質的に半導体素子電極および金属配線を腐食しない。

（ｂ）汚染金属量が１０００～５０００（×10^{10} ａｔｏｍｓ／cm^2）である基板を洗浄した場合に於いて、洗浄後の汚染金属量が１０（×10^{10} ａｔｏｍｓ／cm^2）以下である。

（ｃ）粒径０．１μｍ以上のパーティクルを８０００～１００００（個／０．０３m^2）有する半径ｒの略円形状基板表面をｔ（分）間洗浄した場合に於いて、洗浄後、基板と中心を同じくする基板表面上の円周内でのパーティクル個数が、ｔ＝０．５～１の際、円周半径０．６ｒの円周内で２００／ｔ個以下、または、円周半径０．９ｒの円周内では８００／ｔ個以下である。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、半導体デバイス用基板の洗浄液および洗浄方法に関し、金属汚染やパーティクル汚染が問題となる半導体、ガラス、金属、セラミックス、樹脂、磁性体、超伝導体などの基板表面の洗浄に使用される洗浄液に関する。詳しくは、本発明は、高清浄な基板表面が要求される、半導体素子やディスプレイデバイス用などの半導体デバイス用基板を製造する工程における、半導体デバイス用基板表面を洗浄するための洗浄液および洗浄方法に関する。

【０００２】本発明の洗浄液および洗浄方法は、特に、シリコン等の半導体材料、窒化シリコン、酸化シリコン、ガラス、低誘電率（Ｌｏｗ－ｋ）材料などの絶縁材

料、遷移金属または遷移金属化合物などを表面の一部または全面に有する半導体デバイス用基板に於いて、基板表面に付着したシリカ粒子、アルミナ粒子、有機物粒子の様な微小粒子（パーティクル）、レジスト残渣などの有機汚染、金属汚染を除去し、併せて再付着を抑制し、基板表面の荒れや腐食を引き起こすことなく高度に清浄化することが出来る。

【０００３】

【従来の技術】ＴＦＴ液晶などのフラットパネルディスプレイ、マイクロプロセッサー、メモリー、ＣＣＤ等の半導体デバイスの製造工程では、シリコン、酸化シリコン（SiO_2）、ガラス等の基板表面にサブミクロン乃至クォータミクロンの寸法でパターン形成や薄膜形成を行っている。従って、これらの製造の各工程に於いては、当該基板表面の僅かな汚染も除去し、基板表面を高度に清浄化することが極めて重要な課題となっている。汚染の中でも、特に、微小な汚染であるパーティクル汚染および金属汚染は、その全てを除去することが困難である。しかし、斯かる汚染によって半導体デバイスの電気的特性や歩留まりが低下するため、この様な汚染を次工程に持ち込む前に極力除去する必要がある。そして、この様な汚染の除去には、洗浄液による基板表面の洗浄が一般的に行われている。

【０００４】近年、半導体デバイスの製造に於いては一層のスループット向上、生産効率化が要求されている。そして、益々微細化・高集積化傾向にある半導体デバイス製造用の基板については、基板表面のパーティクル汚染および金属汚染の除去性のみならず除去後の再付着防止性に優れ、且つ、迅速に基板表面を高度に清浄化し得る洗浄液および洗浄方法が望まれている。

【０００５】一般に、パーティクル汚染の除去に使用する洗浄液としては、アルカリ性水溶液が有効であることが知られている。半導体デバイス用基板表面の洗浄には、アンモニア水溶液、水酸化カリウム水溶液、水酸化テトラメチルアンモニウム水溶液などのアルカリ性水溶液が使用されている。また、アンモニア、過酸化水素、水を含む洗浄液（「ＳＣ－１洗浄液」又は「ＡＰＭ洗浄液」という。）による洗浄（「ＳＣ－１洗浄」又は「ＡＰＭ洗浄」という。）も広く使用されている（例えば非特許文献１参照）。

【０００６】そして、最近では、この様なアルカリ性洗浄液の性能を改善すべく、具体的には半導体デバイス用基板表面のエッチングを抑制し、また、表面荒れを抑制し且つ基板表面の濡れ性も向上させ、そして、パーティクル汚染の除去性を向上させること等を目的として、アルカリ性洗浄液に様々な界面活性剤を添加することが種々提案されている。

【０００７】例えば、洗浄液による基板表面の荒れを抑制するため、アルカリ性の過酸化水素水溶液に界面活性剤を添加し、基板表面に対する洗浄液の接触角を１０度以下にすることが提案されている（例えば特許文献１参照）。また、基板表面への洗浄液の濡れ性を向上させるため、エチレンオキサイドの付加モル数が３～１０であるエチレンオキサイド付加型非イオン系界面活性剤を添加した過酸化水素含有アルカリ性洗浄液が提案されている（例えば特許文献２参照）。

【０００８】また、代表的な半導体デバイス基板であるシリコン基板の表面のエッチングを抑制するため、アルカリ性洗浄液に様々な界面活性剤を添加することが提案されている（例えば特許文献３参照）。特に、有機物汚染の除去性能を向上させるために、特定の界面活性剤を含有する半導体デバイス用基板の洗浄に使用する洗浄液が提案されている（例えば特許文献４参照）。汚染除去性向上のため、過酸化水素含有アルカリ性洗浄液にアルキルベンゼンスルホン酸を添加することも提案されている（例えば特許文献５参照）。また、パーティクル除去性向上のため、フルオロアルキルスルホンアミド化合物よりなるフッ素系界面活性剤をＡＰＭ洗浄液に添加することも提案されている（例えば特許文献６参照）。

【０００９】また、半導体デバイス用基板の洗浄に於いては、上記のアルカリ性洗浄液以外に、酸性洗浄液も有用である。一般的に、酸性洗浄液は基板表面の金属汚染除去には有効だが、パーティクル汚染の除去には不向きであることから、パーティクル汚染の除去性向上などを目的として、酸性洗浄液にも様々な界面活性剤を添加することが提案されている。例えば、特定の界面活性剤とフッ化水素酸を使用してシリコンウエーハを洗浄することが提案されている（例えば特許文献７参照）。

【００１０】また、シリコンウエーハの洗浄に使用するフッ酸水溶液に、界面活性剤およびオゾンを添加することが提案されている（例えば特許文献８参照）。金属配線を表面に有する基板に吸着した金属不純物およびパーティクル汚染の除去のため、分散剤および／または界面活性剤に有機酸化合物を添加することも提案されている（例えば特許文献９参照）。

【００１１】また、近年、半導体デバイスの微細化・高積層化に伴い、半導体デバイスにおける微小な半導体素子間を繋ぐ、配線（以下、単に「配線」という。）や、半導体素子における電極（以下、単に「電極」という。）に使用する金属材料として、新たに銅（Ｃｕ）やタングステン（Ｗ）等の新金属材料が導入されつつある。具体的には、例えば、配線材料としては、従来から使用されたきたアルミニウム（Ａｌ）より抵抗値が低いＣｕが採用されつつある。

【００１２】また、他の新規な材料として、積層構造を有する半導体素子間の層間絶縁膜が挙げられる。この層間絶縁膜としては、従来から使用されているSiO_2膜よりも、誘電率の低い、有機ポリマー材料や無機ポリマー材料からなる膜を使用した低誘電率膜が採用されつつある。この層間絶縁膜は、半導体デバイスの製造工程

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中、金属配線がその表面に形成された後に行う基板の洗浄工程（以下、「後工程」ということがある。）の際、配線と共に基板上に露出している。

【００１３】また、電極には、抵抗値が低く微細加工に有利な電極材料として、タングステンが導入されつつある。電極は、通常、金属配線形成前の基板の洗浄工程（以下、「前工程」ということがある。）の際、基板表面上に露出している。従来、前工程に於いて洗浄する基板表面は全てＳｉ化合物で構成されていたので、僅かな汚染でも半導体デバイスに影響が出るために、基板表面を高度に清浄化する必要があった。そのため、ＲＣＡ洗浄による強力な洗浄が必須であった。

【００１４】近年は、上述した様な新材料が表面に露出している様な基板をも、高度に洗浄すべく、先述した様々な提案の適応が試みられている。

【００１５】

【非特許文献１】W. Kern and D. A. Puotinen: RCA Review, p. 187, June (1970)

【特許文献１】特開平５－３３５２９４号公報

【特許文献２】特許第３１６９０２４号公報

【特許文献３】特開２００１－４０３８９号公報

【特許文献４】特開平１１－１２１４１８号公報

【特許文献５】特開平７－２４５２８１号公報

【特許文献６】特開平５－２５１４１６号公報

【特許文献７】特開平７－２１６３９２号公報

【特許文献８】特開平８－６９９９０号公報

【特許文献９】特開２００１－７０７１号公報

【００１６】

【発明が解決しようとする課題】Ａｌ配線を使用した従来の後工程では、Ａｌ配線が強酸や強アルカリに弱いことや、前工程に比べて金属汚染の影響が低いことから、超純水や有機溶媒による簡単な洗浄のみが行われていた。しかし、Ａｌに代わりＣｕを使用すると、以下の様な二つの問題が新たに生じた。

【００１７】第一に、ＣｕはＳｉにとって最も嫌われる汚染物質の一つであり、半導体素子表面の酸化膜（SiO_2膜）中におけるＣｕの拡散速度が速く、その悪影響度はＡｌを遙かに上回ることが問題となっていた。

【００１８】第二に、Ａｌと異なりＣｕはドライエッチングが出来ない点が問題である。Ｃｕによる配線を形成するには、予め（Ｃｕ配線を形成するための）溝を掘った絶縁膜にＣｕめっきを施して配線を形成し、次いで、不要部分をＣＭＰ（Ｃｈｅｍｉｃａｌ　Ｍｅｃｈａｎｉｃａｌ　Ｐｏｌｉｓｈｉｎｇ）等の方法によって削り取る方法、所謂ダマシン法による配線形成をせざるを得ない。

【００１９】上記のダマシン法による配線形成では大量のＣｕと、ＣＭＰに使用したスラリー中の研磨粒子（酸化アルミニウム粒子などに代表されるパーティクル）が、Ｃｕ配線や低誘電率膜表面を汚染してしまうことが

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問題となる。この様な基板表面の汚染は、もはや超純水や有機溶媒による簡単な洗浄では除去できず、深刻な問題となっていた。

【００２０】上記の様な汚染に対して、強酸や強アルカリによる従来のＲＣＡ洗浄を行うと、ＣｕやW等の新金属材料は過酸化水素に対して溶解してしまうという問題が新たに生じていた。そして、更に、低誘電率膜表面は疎水性なので洗浄液の濡れ性が悪く、洗浄液をはじいてしまい、特に、パーティクル汚染の除去を充分に除去し難いという問題がある。

【００２１】従って、上記の様な新材料を表面に有する基板の洗浄工程では、今後、過酸化水素水を含有する、ＲＣＡ洗浄液を使用した洗浄が不可能となる等、深刻な問題が生じており、過酸化水素などの薬液に弱い新金属材料を表面に有する基板を洗浄するに当たり、新たな洗浄液の開発が強く望まれている。

【００２２】これに対し、前述した様に、界面活性剤を含有する洗浄液の開発がなされてきた。しかし、金属汚染除去やパーティクル汚染除去と共に、再付着防止が充分になされ、且つ、下記（１）～（３）に記載の課題を満足する洗浄液は、これ迄になく、基板の表面洗浄に於ける課題となっていた。

【００２３】（１）室温あるいは加温時に、界面活性剤が洗浄液中に油滴となって析出・白濁することなく、洗浄性能の低下や、基板表面への油滴の残留などを引き起こさないこと。

（２）発泡性が小さく、洗浄装置の動作に悪影響を与えないこと。

（３）界面活性剤が自然環境に悪影響を与えない物質であり、洗浄廃液が適切に処理できること。

【００２４】例えば、アニオン系界面活性剤は、一般的に曇点が無いので、高い洗浄効果を期待して洗浄液の温度を高く（例えば８０℃以上）して使用することが可能である。しかし、高発泡性であるので洗浄装置での操作性に悪影響を及ぼす恐れがある。

【００２５】また、非イオン系界面活性剤は、洗浄性能が高く、低発泡性ではあるが、曇点は一般的に低い。従って、高い洗浄効果を期待し、洗浄液の温度を高くして洗浄を行うと、この界面活性剤が洗浄液中に油滴状として現れ、基板上に残留するという問題がある。

【００２６】

【課題を解決するための手段】本発明者らは、上述した課題につき、界面活性剤を使用する半導体デバイス用基板洗浄液について鋭意検討した。特に、洗浄液に使用する界面活性剤、とりわけ非イオン系界面活性剤であるエチレンオキサイド型界面活性剤に着目した。

【００２７】エチレンオキサイド型界面活性剤は、炭化水素基とポリオキシエチレン基を同一分子構造内に有するものである。本発明者らは、この様な構造のエチレンオキサイド型界面活性剤に於いて、炭化水素基に含まれ

る炭素数（m）とポリオキシエチレン基中のオキシエチレン基の数（n）との比率（m／n）が１～１．５、炭素数（m）が９以上、ポリオキシエチレン基中のオキシエチレン基数（n）が７以上の条件を満たす特定範囲内の界面活性剤に着目した。

【００２８】この特定範囲内のエチレンオキサイド型界面活性剤の多くは、室温、大気圧の条件下に於いて、固体であり且つ水への溶解度が低い。故に、この様なエチレンオキサイド型界面活性剤は、工業的生産工程に於いて取り扱い性が低く、使用が避けられていた。しかし、この様な、特定範囲内のエチレンオキサイド型界面活性剤を加熱溶融させ、水に溶解させて調製した、アルカリ又は有機酸を含有する半導体デバイス用基板洗浄液は、意外にも、実質的に過酸化水素を含有せずとも、良好な洗浄性能を示した。とりわけ、一般的な汚染洗浄効果からは予測できない、微小粒子汚染に対する洗浄性（粒径０．１μmオーダーのパーティクル除去性）に優れていた。しかも、上記の半導体デバイス用基板洗浄液は、疎水性のために水性洗浄液をはじき易く、パーティクル除去性が低い低誘電率膜表面へも、充分な濡れ性を示し、優れた洗浄効果を奏した。本発明者らは、これらのことを見出し、本発明を完成させるに至った。

【００２９】すなわち、本発明の要旨は、少なくとも、以下の成分（A）、（B）及び（C）を含有することを特徴とする半導体デバイス用基板の洗浄液および当該洗浄液を使用する洗浄方法に存する。

【００３０】成分（A）：置換基（フェニル基を除く）を有していてもよい炭化水素基とポリオキシエチレン基とを有し、炭化水素基中の炭素数（m）とポリオキシエチレン基中のオキシエチレン基数（n）の比率（m／n）が１～１．５であり、炭素数（m）が９以上、オキシエチレン基数（n）が７以上であるエチレンオキサイド型界面活性剤。

成分（B）：水

成分（C）：アルカリ又は有機酸

【００３１】

【発明の実施の形態】以下、本発明を詳細に説明する。本発明の洗浄液は、少なくとも、成分（A）として特定の界面活性剤、成分（B）として水、成分（C）としてアルカリ又は有機酸を含有する。

【００３２】本発明に於いて、成分（A）として使用する界面活性剤は、置換基（フェニル基を除く）を有していてもよい炭化水素基とポリオキシエチレン基とを有し、炭化水素基中の炭素数（m）とポリオキシエチレン基中のオキシエチレン基数（n）の比率（m／n）が１～１．５であり、炭素数（m）が９以上、オキシエチレン基数（n）が７以上であるエチレンオキサイド型界面活性剤である。

【００３３】上記の比率（m／n）が１未満の場合は、液中におけるパーティクル除去能力やシリコンの腐食抑制が不十分となる。また、オキシエチレン鎖長増による水への溶解性の低下、廃液処理の負荷も増加する。一方、１．５を超える場合は、アルカリ液中で洗浄時にO／W型のエマルジョンを形成し、界面活性剤が細かい油滴となって析出して白濁してしまい、洗浄性能の低下や油滴の残留などの問題を引き起こす。比率（m／n）は、好ましくは１～１．４である。

【００３４】上記の炭素数（m）が９未満の場合は、（m／n）比が前記最適範囲内であってもパーティクル除去性が低下する。また、（m）が大きすぎる場合は、水への溶解性の低下や廃液処理の負荷も増加するので好ましくない。従って、炭素数（m）は、好ましくは９～１６、更に好ましくは１０～１４である。ただし、成分（A）を構成する炭化水素基が、置換基として炭化水素基を有する際には、主鎖となる炭化水素基と、置換基である炭化水素基における炭素数の合計数をmとする。

【００３５】また、上記の（n）が７未満の場合は、（m／n）比が前記最適範囲内であってもパーティクル除去性が低下する。（n）が大きすぎる場合は、廃液処理の負荷が大きくなり、また、界面活性剤が洗浄液中で分解し易くなる。従って、（n）は、好ましくは７～１６、更に好ましくは７～１４である。

【００３６】本発明で規定する上記のエチレンオキサイド型界面活性剤を使用することにより、洗浄液の濡れ性とパーティクルの除去性の両方が良くなる。上記のエチレンオキサイド型界面活性剤としては、例えば、ポリオキシエチレンアルキルエーテル、ポリオキシエチレン脂肪酸エステル、ポリオキシエチレンアルキルアミン、ポリオキシエチレンアルキルエーテル硫酸塩などが挙げられる。特に、パーティクル汚染の除去性や再付着防止能などの観点から、下記一般式（II）で表されるポリオキシエチレンアルキルエーテルが好ましい。

【００３７】

【化２】$R^2O-(CH_2CH_2O)_nH$　　(II)

（但し、R^2は、水酸基、アミノ基、アルコキシ基、ハロゲンにて置換されていてもよいアルキル基を示し、アルキル基に含まれる炭素数（m）は９以上であり、（n）は７以上の数を表す。）

【００３８】上記のポリオキシエチレンアルキルエーテルの具体例としては、ポリオキシエチレン（n＝８）ノニルエーテル、ポリオキシエチレン（n＝９）デシルエーテル、ポリオキシエチレン（n＝１１）ウンデシルエーテル、ポリオキシエチレン（n＝１０）ラウリルエーテル、ポリオキシエチレン（n＝１１）ラウリルエーテル、ポリオキシエチレン（n＝１０）トリデシルエーテル、ポリオキシエチレン（n＝１２）トリデシルエーテル、ポリオキシエチレン（n＝１１）テトラデシルエーテル、ポリオキシエチレン（n＝１３）テトラデシルエーテル、ポリオキシエチレン（n＝１２）ペンタデシルエーテル、ポリオキシエチレン（n＝１４）ペンタデシ

ルエーテル、ポリオキシエチレン（ｎ＝１２）セチルエーテル、ポリオキシエチレン（ｎ＝１５）セチルエーテル、ポリオキシエチレン（ｎ＝１８）オレイルエーテル等が挙げられる。なお、上記のｎにおける数値は前記の一般式（II）におけるｎを表す。

【００３９】本発明に於いては、本発明の範囲内であれば（ｍ）及び（ｎ）の異なる複数のエチレンオキサイド型界面活性剤を任意の割合で併用してもよい。更に複数種の界面活性剤を併用する際、全界面活性剤の（ｍ／ｎ）の平均値が１～１．５、（ｍ）の平均値が９以上、（ｎ）の平均値が７以上の条件を満たせば、各々個別の界面活性剤に於いて（ｍ／ｎ）が１．０未満または１．５を超えていても、また、（ｍ）が９未満、（ｎ）が７未満であってもよい。

【００４０】洗浄液中における成分（Ａ）の含有量は、通常０．０００１～１重量％、好ましくは０．０００３～０．５重量％、更に好ましくは０．００１～０．１重量％、特に好ましくは０．００１～０．０５重量％である。成分（Ａ）の濃度が低すぎる場合は、パーティクル汚染除去性能が十分でなく、一方、成分（Ａ）の濃度が高すぎる場合は、パーティクル汚染の除去性能に変化がなく、泡立ちが顕著となり洗浄工程に不向きとなったり、また、廃液を生分解処理する場合の負荷が増大する場合がある。

【００４１】成分（Ａ）は、通常販売されている形態に於いて１～数千ｐｐｍ程度のＮａ、Ｋ、Ｆｅ等の金属不純物が含有している場合がある。斯かる場合は、成分（Ａ）が金属汚染源となる。そのため、成分（Ａ）として使用する界面活性剤は、精製して使用するのが好ましい。そして、金属不純物各々の含有量は、通常１０ｐｐｍ以下、好ましくは１ｐｐｍ以下、更に好ましくは０．１ｐｐｍ以下とされる。精製方法としては、例えば、界面活性剤を水で溶解した後、イオン交換樹脂に通液し、樹脂に金属不純物を捕捉させる方法が好適である。

【００４２】上記の様に精製された成分（Ａ）を使用することで、金属不純物含有量が極めて低減された洗浄液を得ることが出来る。本発明の洗浄液としては、洗浄液中の金属不純物のうち、少なくとも、Ｎａ、Ｍｇ、Ａｌ、Ｋ、Ｃａ、Ｆｅ、Ｃｕ、Ｐｂ、Ｚｎの各々の含有量が、２０ｐｐｂ以下、中でも５ｐｐｂ以下、特に０．１ｐｐｂ以下であることが好ましい。

【００４３】なお、本発明に於いては、本発明の効果を損ねない範囲で成分（Ａ）以外の界面活性剤を使用してもよい。成分（Ａ）以外の界面活性剤としては、カチオン系界面活性剤、アニオン系界面活性剤およびノニオン系界面活性剤の何れでもよい。中でも、アニオン系界面活性剤やノニオン系界面活性剤を使用することが好ましく、具体的には、例えば、アニオン系界面活性剤としては、炭素数８～１２のアルキ ルベンゼンスルホン酸およびその塩、炭素数８～１２のアルキルメチルタウリン酸 およびその塩、炭素数８～１２のアルキル硫酸エステル及びその塩などが挙げられ る。ノニオン系界面活性剤としては、ポリオキシアルキレンのみからなる界面活 性剤などが挙げられる。

【００４４】本発明に於いては、成分（Ｂ）として水を使用する。高清浄な基板表面を得たい場合は、通常、脱イオン水、好ましくは超純水が使用される。また、水の電気分解によって得られる電解イオン水、水に水素ガスを溶存させた水素水などを使用することも出来る。

【００４５】本発明に於いては、成分（Ｃ）としてアルカリ又は有機酸を使用する。すなわち、本発明の洗浄液はアルカリ性洗浄液または酸性洗浄液とされる。

【００４６】本発明で使用されるアルカリの種類は、特に限定されないが、代表的なアルカリとしては、水酸化アンモニウム（アンモニア水溶液）と有機アルカリが挙げられる。有機アルカリとしては、水酸化第４級アンモニウム、アミン、アミノアルコール等のアミン類が挙げられる。水酸化第４級アンモニウムとしては、水酸基、アルコキシ基、ハロゲンにて置換されていてもよい炭素数１～４のアルキル基または炭素数１～４のヒドロキシアルキル基を有するものが好ましく、これらの置換基は全て同一でも異なっていてもよい。

【００４７】上記の様なアルキル基としては、メチル基、エチル基、プロピル基、ブチル基などの炭素数１～４の低級アルキル基が挙げられ、ヒドロキシアルキル基としては、ヒドロキシメチル基、ヒドロキシエチル基、ヒドロキシプロピル基、ヒドロキシブチル基などの炭素数１～４の低級ヒドロキシアルキル基が挙げられる。

【００４８】上記の置換基を有する水酸化第４級アンモニウムの具体例としては、テトラメチルアモニウムヒドロキシド（ＴＭＡＨ）、テトラエチルアンモニウムヒドロキシド、トリメチル（ヒドロキシエチル）アンモニウムヒドロキシド（通称：コリン）、トリエチル（ヒドロキシエチル）アンモニウムヒドロキシド等が挙げられる。一方、アミン類としては、エチレンジアミン、モノエタノールアミン、トリメタノールアミン等が挙げられる。

【００４９】上述のアルカリの中では、洗浄効果、金属残留が少ないこと、経済性、洗浄液の安定性などの理由から、水酸化アンモニウム、テトラメチルアンモニウムヒドロキシド（ＴＭＡＨ）、トリメチル（ヒドロキシエチル）アンモニウムヒドロキシド（通称：コリン）が好ましい。これらのアルカリは、単独で使用してもよいし、２種以上を任意の割合で使用してもよい。

【００５０】洗浄液中のアルカリの濃度は、適宜選択すればよいが、洗浄液のｐＨが９以上のアルカリ性となる濃度であることが好ましい。アルカリ濃度が低すぎてｐＨが高くない場合は、本発明の目的である汚染除去効果が得られない場合がある。一方、ｐＨが高すぎる場合は、ｐＨを高めたことによる効果が得られずに経済的に

不利であるばかりか、基板表面がエッチングにより損傷する危険性が増すので好ましくない。従って、アルカリ性洗浄液のｐＨは、好ましくは９～１３、更に好ましくは１０～１２．５、特に好ましくは１０．５～１２である。

【００５１】本発明で使用される有機酸の種類は、特に限定されないが、有機カルボン酸または有機スルホン酸が好ましい。有機カルボン酸の代表的なものとしては、蟻酸、酢酸、プロピオン酸、酪酸、イソ酪酸、吉草酸、エチルメチル酢酸、トリメチル酢酸、蓚酸、コハク酸、マロン酸、クエン酸、酒石酸、リンゴ酸などが挙げられる。これらの中では、酢酸、プロピオン酸、蓚酸、コハク酸、マロン酸、クエン酸、酒石酸、リンゴ酸の群から選択される１種または２種以上が好ましく、酢酸、蓚酸、クエン酸の群から選択される１種または２種以上が更に好ましい。酢酸は、半導体基板のエッチャント材料などに使用されており、蒸留操作により高純度で金属不純物の少ない物が安価で入手が可能であり、水分蒸発による粉体の発生も起こらない点で最も好ましい。

【００５２】有機スルホン酸の代表的なものとしては、メタンスルホン酸、エタンスルホン酸、ｎ－プロパンスルホン酸、ｉ－プロパンスルホン酸、ｎ－ブタンスルホン酸、フェニルスルホン酸などが挙げられる。これらの中では、メタンスルホン酸および／またはエタンスルホン酸が好ましく、メタンスルホン酸が特に好ましい。上記の有機酸は、単独で使用してもよいし、２種以上を任意の割合で使用してもよい。

【００５３】洗浄液中の有機酸の濃度は、適宜選択すればよいが、酸性洗浄液のｐＨが１～５となる濃度であることが好ましい。有機酸の濃度が低すぎてｐＨが充分低くない場合は、本発明の目的である汚染の除去や付着防止効果が得られない場合がある。一方、濃度が高すぎる場合は、ｐＨを低下させたことによる効果が得られずに経済的に不利で有るばかりか、基板表面の腐食の原因にもなり得るので好ましくない。酸性洗浄液のｐＨは好ましくは２～３である。

【００５４】本発明の洗浄液に於いては、錯化剤を含有させると基板表面の金属汚染を更に低減した極めて高度に清浄化された表面が得られるので好ましい。錯化剤としては、従来公知の任意のものを使用できる。錯化剤の種類は、基板表面の汚染レベル、金属の種類、基板表面に要求される清浄度レベル、錯化剤コスト、化学的安定性などから総合的に判断して選択すればよく、例えば、以下の（１）～（４）にて示すものが挙げられる。

【００５５】（１）ドナー原子である窒素とカルボキシル基および／またはホスホン酸基を有する化合物：例えば、グリシン等のアミノ酸類；イミノ２酢酸、ニトリロ３酢酸、エチレンジアミン４酢酸［ＥＤＴＡ］、トランス－１，２－ジアミノシクロヘキサン４酢酸［ＣｙＤＴＡ］、ジエチレントリアミン５酢酸［ＤＴＰＡ］、トリエチレンテトラミン６酢酸［ＴＴＨＡ］等の含窒素カルボン酸類；エチレンジアミンテトラキス（メチレンホスホン酸）［ＥＤＴＰＯ］、ニトリロトリス（メチレンホスホン酸）［ＮＴＰＯ］、プロピレンジアミンテトラ（メチレンホスホン酸）［ＰＤＴＭＰ］等の含窒素ホスホン酸類などが挙げられる。

【００５６】（２）芳香族炭化水素環を有し且つ芳香族炭化水素環を構成する炭素原子に直接結合したＯＨ基および／またはO^-基を２つ以上有する化合物：例えば、カテコール、レゾルシノール、タイロン等のフェノール類、その誘導体などが挙げられる。

【００５７】（３）上記（１）及び（２）の構造を併せ持った化合物：

【００５８】（３－１）エチレンジアミンジオルトヒドロキシフェニル酢酸［ＥＤＤＨＡ］及びその誘導体：例えば、エチレンジアミンジオルトヒドロキシフェニル酢酸［ＥＤＤＨＡ］、エチレンジアミン－Ｎ，Ｎ’－ビス〔（２－ヒドロキシ－５－メチルフェニル）酢酸〕［ＥＤＤＨＭＡ］、エチレンジアミン－Ｎ，Ｎ’－ビス〔（２－ヒドロキシ－５－クロルフェニル）酢酸〕［ＥＤＤＨＣＡ］、エチレンジアミン－Ｎ，Ｎ’－ビス〔（２－ヒドロキシ－５－スルホフェニル）酢酸〕［ＥＤＤＨＳＡ］等の芳香族含窒素カルボン酸類；エチレンジアミン－Ｎ，Ｎ’－ビス〔（２－ヒドロキシ－５－メチルフェニル）ホスホン酸〕、エチレンジアミン－Ｎ，Ｎ’－ビス〔（２－ヒドロキシ－５－ホスホフェニル）ホスホン酸〕等の芳香族含窒素ホスホン酸類が挙げられる。

【００５９】（３－２）Ｎ，Ｎ’－ビス（２－ヒドロキシベンジル）エチレンジアミン－Ｎ，Ｎ’－２酢酸［ＨＢＥＤ］及びその誘導体：例えば、Ｎ，Ｎ’－ビス（２－ヒドロキシベンジル）エチレンジアミン－Ｎ，Ｎ’－２酢酸［ＨＢＥＤ］、Ｎ，Ｎ’－ビス（２－ヒドロキシ－５－メチルベンジル）エチレンジアミン－Ｎ，Ｎ’－２酢酸［ＨＭＢＥＤ］、Ｎ，Ｎ’－ビス（２－ヒドロキシ－５－クロルベンジル）エチレンジアミン－Ｎ，Ｎ’－２酢酸などが挙げられる。

【００６０】（４）その他：例えば、エチレンジアミン、８－キノリノール、ｏ－フェナントロリン等のアミン類；ギ酸、酢酸、シュウ酸、酒石酸などのカルボン酸類；フッ化水素酸、塩酸、臭化水素、ヨウ化水素などのハロゲン化水素、それらの塩；リン酸、縮合リン酸などのオキソ酸類、それらの塩などが挙げられる。

【００６１】上記の錯化剤は、酸の形態のものを使用してもよいし、アンモニウム塩などの塩の形態のものを使用してもよい。

【００６２】上述した錯化剤の中でも、洗浄効果、化学的安定性などの理由から、エチレンジアミン４酢酸［ＥＤＴＡ］、ジエチレントリアミン５酢酸［ＤＴＰＡ］等の含窒素カルボン酸類；エチレンジアミンテトラキス

（メチレンホスホン酸）［ＥＤＴＰＯ］、プロピレンジアミンテトラ（メチレンホスホン酸）［ＰＤＴＭＰ］等の含窒素ホスホン酸類；エチレンジアミンジオルトヒドロキシフェニル酢酸［ＥＤＤＨＡ］及びその誘導体；Ｎ，Ｎ’－ビス（２－ヒドロキシベンジル）エチレンジアミン－Ｎ，Ｎ’－２酢酸［ＨＢＥＤ］が好ましい。

【００６３】中でも洗浄効果の観点からエレンジアミンジオルトヒドロキシフェニル酢酸［ＥＤＤＨＡ］、エチレンジアミン－Ｎ，Ｎ’－ビス｛（２－ヒドロキシ－５－メチルフェニル）酢酸｝［ＥＤＤＨＭＡ］、ジエチレントリアミン５酢酸［ＤＴＰＡ］、エチレンジアミン４酢酸［ＥＤＴＡ］、プロピレンジアミンテトラ（メチレンホスホン酸）［ＰＤＴＭＰ］が好ましい。上記の錯化剤は、単独で使用してもよいし、２種以上を任意の割合で使用してもよい。

【００６４】洗浄液中の錯化剤の濃度は、汚染金属不純物の種類と量、基板表面に要求される清浄度レベルによって任意に選択すればよいが、通常１～１００００ｐｐｍ、好ましくは５～１０００ｐｐｍ、更に好ましくは１０～２００ｐｐｍである。錯化剤の濃度が低すぎる場合は、錯化剤による汚染除去や付着防止効果が得られず、高すぎる場合は、濃度増加に見合う効果が得られずに経済的に不利であるばかりか、基板表面に錯化剤が付着し、表面処理後に残留する危険性が増す。

【００６５】なお、錯化剤は、通常販売されている試薬に於いて１～数千ｐｐｍ程度のＦｅＡｌ、Ｚｎ等の金属不純物を含有しているので、本発明で使用する錯化剤が金属汚染源となる場合が考えられる。これらの金属は、初期には錯化剤と安定な錯体を形成して存在しているが、表面洗浄液として長時間使用しているうちに錯化剤が分解してくると、遊離し、基板表面に付着する。そのため、本発明で使用する錯化剤は、予め、精製して使用するのが好ましい。そして、含まれる金属不純物各々の含有量は、通常５ｐｐｍ以下、好ましくは１ｐｐｍ以下、更に好ましくは０．１ｐｐｍ以下とされる。精製方法としては、例えば、酸性またはアルカリ性溶液に錯化剤を溶解した後、不溶性不純物をろ過分離して取り除き、再び中和して結晶を析出させ、当該結晶を液と分離する方法が好適である。

【００６６】また、本発明の洗浄液は、その性能を損なわない範囲に於いて、その他の成分を任意の割合で含有していてもよい。他の成分としては、含硫黄有機化合物（２－メルカプトチアゾリン、２－メルカプトイミダゾリン、２－メルカプトエタノール、チオグリセロール等）、含窒素有機化合物（ベンゾトリアゾール、アルキルベンゾトリアゾール、テトラソール、３－アミノトリアゾール、Ｎ（Ｒ）$_3$（Ｒは炭素数１～４のアルキル基）、Ｎ（ＲＯＨ）$_3$（Ｒは炭素数１～４のアルキル基）、ウレア、チオウレア等）、水溶性ポリマー（ポリエチレングリコール、ポリビニルアルコール等）、アルキルアルコール系化合物（ＲＯＨ（Ｒは炭素数１～４のアルキル基））等の防食剤、硫酸、塩酸などの酸、ヒドラジン等の還元剤、水素、アルゴン、窒素などの溶存ガス、フッ酸、フッ化アンモニウム、ＢＨＦ等のドライエッチング後に強固に付着したポリマー等の除去効果が期待できるエッチング促進剤などが挙げられる。

【００６７】そして、本発明の洗浄液に含有させる他の成分として過酸化水素、オゾン、酸素などの酸化剤も挙げられる。半導体デバイス用基板の洗浄工程に於いて、酸化膜のないシリコン（ベアシリコン）基板表面を洗浄する際には、酸化剤の配合により、基板表面へのエッチングによる表面荒れを抑えることが出来るので好ましい。本発明のアルカリ性洗浄液に過酸化水素を含有させる場合には、洗浄液中の過酸化水素濃度は、通常０．０１～５重量％、好ましくは０．１～１重量％とされる。

【００６８】ところで、洗浄する基板の表面には、過酸化水素と反応して溶解する金属材料からなる半導体デバイスの配線やデバイス素子電極が露出している場合がある。この様な金属材料としては、例えば、ＣｕやＷなどの遷移金属または遷移金属化合物が挙げられる。この際、洗浄に使用する洗浄液は、実質的に過酸化水素を含有しないことが好ましい。本発明の洗浄液は、従来のＡＰＭ洗浄液とは異なり、過酸化水素を実質的に含有しなくても、この様な金属材料に悪影響を及ぼすことなく、充分な洗浄性能を示す。

【００６９】なお、本発明の洗浄液に於いて、「実質的に過酸化水素を含有しない」とは、洗浄する基板上の材料、例えばＣｕやＷ等の配線材料や電極材料、及び低誘電率膜に対し、過酸化水素による腐食や変質などの悪影響を生じさせないことを意味する。つまり、これらの材料が、半導体デバイスとした際に、配線や電極などとして充分に機能することを意味する。そのためには、本発明の洗浄液に過酸化水素が含まれない様にし、含有されたとしてもその含有量を少なく抑えるほど好ましい。その含有量は、例えば、１０ｐｐｍ以下、好ましくは１ｐｐｍ、更に好ましくは１０ｐｐｂ以下とされる。

【００７０】本発明の洗浄液は、金属汚染やパーティクル汚染が問題となる半導体、ガラス、金属、セラミックス、樹脂、磁性体、超伝導体などの基板表面の洗浄に使用される。特に高清浄な基板表面が要求される、半導体素子、ディスプレイデバイス用などの半導体デバイス用基板を製造する工程における、半導体デバイス用基板表面の洗浄に好適に使用される。これらの基板の表面には、配線、電極などが存在していてもよい。配線や電極の材料としては、Ｓｉ、Ｇｅ、ＧａＡｓ等の半導体材料；SiO_2、窒化シリコン、ガラス、低誘電率材料、酸化アルミニウム、遷移金属酸化物（酸化チタン、酸化タンタル、酸化ハフニウム、酸化ジルコニウム等）、（Ｂａ、Ｓｒ）TiO_3（ＢＳＴ）、ポリイミド、有機熱硬化性樹脂などの絶縁材料；Ｗ、Ｃｕ、Ａｌ等の金属

またはこれらの合金、シリサイド、窒化物などが挙げられる。低誘電率材料とは、比誘電率が３．５以下である材料の総称である。因に、SiO_2の比誘電率は３．８～３．９である。

【００７１】特に、本発明の洗浄液は、表面に遷移金属または遷移金属化合物を有する半導体デバイス用基板の洗浄に好適に使用される。遷移金属としては、Ｗ、Ｃｕ、Ｔｉ、Ｃｒ、Ｃｏ、Ｚｒ、Ｈｆ、Ｍｏ、Ｒｕ、Ａｕ、Ｐｔ、Ａｇ等が挙げられ、遷移金属化合物としては、これらの遷移金属のチッ化物、酸化物、シリサイド等が挙げられる。これらの中では、Ｗ及び／又はＣｕが好ましい。

【００７２】表面にタングステンを有する基板の洗浄を行う工程としては、タングステンをゲート電極材料として使用した場合の、ゲート電極とシリコン等を有する基板表面の洗浄が挙げられる。具体的には、半導体デバイスにタングステン膜を形成した後の洗浄工程、特に、タングステン膜をドライエッチングした後の洗浄工程、その後にシリコン露出部にイオン注入した後の洗浄工程が挙げられる。

【００７３】本発明の洗浄液を使用すれば、超音波照射やブラシスクラブを行わなくても、パーティクルや金属の除去を行なうことが出来る。従って、本発明の洗浄液は、超音波洗浄やブラシスクラブを行うと壊れてしまう恐れが大きい、極微細な（例えば、ゲート電極の幅が０．１５μｍ程度の）ゲート電極をタングステンで形成した場合の、ゲート電極および基板表面の洗浄に好適である。

【００７４】表面にＣｕを有する基板の洗浄を行う工程としては、Ｃｕを配線材料として使用した場合の、Ｃｕ配線と層間絶縁膜などを有する基板表面の洗浄が挙げられる。具体的には、半導体デバイスにＣｕ膜を形成した後の洗浄工程、特にＣｕ膜に対してＣＭＰ（Chemical Mechanical Polishing）を行った後の洗浄工程、配線上の層間絶縁膜にドライエッチングによりホールを開けた後の洗浄工程が挙げられる。

【００７５】また、本発明の洗浄液は、表面に層間絶縁膜材料となる低誘電率材料を有する半導体デバイス用基板の洗浄にも好適に使用される。低誘電率材料としては、有機ポリマー材料、無機ポリマー（シロキサン系）材料、多孔質（ポーラス）材料と、大きく３つに分けられる。有機ポリマー材料としては、Polyimide、ＢＣＢ(Benzocyclobutene)、Flare(Honeywell社)、SiLK(Dow Chemical)等が挙げられ、無機ポリマー材料としては、ＦＳＧ(Fluorinated silicate glass)、BLACK DIAMOND(Applied Materials)、Aurora(日本ASM)等が挙げられる。

【００７６】本発明の洗浄液は、上述の様に、基板表面に於ける電極や配線材料の有無に拘わらず、半導体デバイス用基板の表面洗浄に好適に使用される。その中でも、本発明の洗浄液は、基板表面に於ける水の接触角が

６０°以上の疎水性を示す半導体デバイス用基板の洗浄に好適に使用される。

【００７７】本発明の洗浄液の調製方法は、従来公知の方法によればよい。洗浄液の構成成分（例えば、界面活性剤、水酸化アンモニウム、水、必要に応じて錯化剤など、他の成分）のうち、何れか２成分または３成分以上を予め配合し、その後に残りの成分を混合してもよいし、一度に全部を混合してもよい。

【００７８】前述の様に、本発明の半導体デバイス用基板洗浄液は、今後の新材料、つまり過酸化水素などの薬液に対して耐性の低い金属材料が表面にある半導体デバイス用基板でも、これら新材料を実質的に腐食しないので、前工程および後工程の何れにも使用可能な、優れた洗浄効果を奏する洗浄液となる。

【００７９】すなわち、本発明の他の要旨は、以下の条件（ａ）、（ｂ）及び（ｃ）を満たすことを特徴とする、少なくとも半導体素子電極または金属配線を表面に有する、半導体デバイス用基板洗浄液に存する。

【００８０】（ａ）実質的に半導体素子電極および金属配線を腐食しない。

（ｂ）汚染金属量が１０００～５０００（$\times 10^{10}$ atoms／cm^2）である基板を洗浄した場合に於いて、洗浄後の汚染金属量が１０（$\times 10^{10}$ atoms／cm^2）以下である。

（ｃ）粒径０．１μｍ以上のパーティクルを８０００～１００００（個／０．０３m^2）有する半径ｒの略円形状基板表面をｔ（分）間洗浄した場合に於いて、洗浄後、基板と中心を同じくする基板表面上の円周内でのパーティクル個数が、ｔ＝０．５～１の際、円周半径０．６ｒの円周内で２００／ｔ個以下、または、円周半径０．９ｒの円周内では８００／ｔ個以下である。

【００８１】なお、上記の（ｂ）及び（ｃ）の規定は、本発明の洗浄液の特性を規定したものであり、本発明の洗浄液が使用される洗浄条件を規定したものではない。また、本発明の洗浄液に於いて、「実質的に半導体素子電極及び金属配線を腐食しない」とは、洗浄する基板上の半導体素子電極や金属配線、具体的には、例えばＷやＣｕ等の電極材料や配線材料に対して、腐食や変質などの悪影響を生じさせず、これらの材料が、半導体デバイスとした際に、電極や配線などとして充分に機能することを意味する。

【００８２】上記の本発明の洗浄液に於いて、条件（ｂ）及び（ｃ）を満たすということは、金属汚染、パーティクル汚染、何れの汚染をも充分に除去することが可能であることを示す。

【００８３】条件（ｃ）は、洗浄対象が略円板状基板の表面、つまり略円形状基板表面の際、短時間の洗浄であっても、基板表面の位置によらず、基板表面を高度に清浄化出来ることを意味する。つまり粒径０．１μｍ以上のパーティクルを８０００～１００００（個／０．０

３m^2）有する半径ｒの略円形状基板表面を洗浄時間ｔ：０．５～１［分］として洗浄した後、基板と中心を同じくする基板表面上の比較的内周部である円周半径０．６ｒの円周内では、残留するパーティクルを２００／ｔ個以下まで除去し、且つ、比較的外周部までをも含む円周半径０．９ｒの円周内に於いても、パーティクルを８００／ｔ個以下とし、基板表面を高度に清浄化できることを意味する。

【００８４】また、上述した、本発明の半導体デバイス用基板洗浄液における、「洗浄した場合に於いて」とは、後述する様な洗浄方法によって、半導体デバイス用基板を洗浄液によって洗浄した場合であることを示す。洗浄方法は、通常、半導体デバイス用基板の洗浄時に採用されうる方法であれば特に限定されない。中でも、洗浄液の基板への接触方法は、基板上に洗浄液を流しながら基板を高速回転させるスピン式とし、洗浄液の液温度は室温～９０℃の範囲とすることが安定した結果が得られるので好ましい。

【００８５】更に、洗浄の際、物理力による洗浄方法、例えば洗浄ブラシを使用したスクラブ洗浄などの機械的洗浄や、基板に周波数０．５メガヘルツ以上の超音波を照射する超音波洗浄、そしてこれらを併用する洗浄方法などを採用することにより、より安定した洗浄結果が得られるので好ましい。

【００８６】本発明の洗浄方法は、洗浄液を基板に直接接触させる方法で行われる。洗浄液の基板への接触方法には、洗浄槽に洗浄液を満たして基板を浸漬させるディップ式、ノズルから基板上に洗浄液を流しながら基板を高速回転させるスピン式、基板に液を噴霧して洗浄するスプレー式などが挙げられる。この様な洗浄を行うための装置としては、カセットに収容された複数枚の基板を同時に洗浄するバッチ式洗浄装置、１枚の基板をホルダーに装着して洗浄する枚葉式洗浄装置などがある。

【００８７】洗浄時間は、バッチ式洗浄装置の場合、通常３０秒から３０分、好ましくは１～１５分、枚葉式洗浄装置の場合、通常１秒から１５分、好ましくは５秒から５分である。洗浄時間が短すぎる場合は洗浄効果が十分でなく、長すぎる場合は、洗浄効果の向上は小さく、スループットの低下を招く。本発明の洗浄液は、上記の何れの方法にも適用できるが、短時間でより効率的な汚染除去が出来る点から、スピン式やスプレー式の洗浄に好ましく使用される。そしては、洗浄時間の短縮、洗浄液使用量の削減が問題となっている枚葉式洗浄装置に適用するならば、これらの問題が解消されるので好ましい。

【００８８】洗浄液の温度は、通常は室温とされるが、洗浄効果を向上させる目的で、４０～７０℃程度に加温

することが好ましい。更に、表面にシリコンが露出している基板を洗浄する場合は、シリコン表面に有機物汚染が残留し易いため、基板を温度３００℃以上の加熱処理工程に供して熱分解させるか、または、オゾン水処理によって有機物を酸化分解処することが好ましい。

【００８９】また、本発明の洗浄方法は、物理力による洗浄方法、例えば、洗浄ブラシを使用したスクラブ洗浄などの機械的洗浄や超音波洗浄と併用させることが好ましい。特に、超音波照射またはブラシスクラブを併用するならば、パーティクル汚染の除去性が更に向上し、洗浄時間の短縮にも繋がるので好ましい。特に、ＣＭＰ後の洗浄で樹脂製ブラシを使用して洗浄するのが好ましい。

【００９０】樹脂製ブラシの材質は、任意に選択し得るが、例えばＰＶＡ（ポリビニルアルコール）を使用するのが好ましい。また、基板に周波数０．５メガヘルツ以上の超音波を照射するならば、界面活性剤との相乗作用により、パーティクルの除去性が著しく向上するので好ましい。更に、本発明の洗浄方法の前および／または後に、水の電気分解によって得られる電解イオン水、または、水に水素ガスを溶存させた水素水による洗浄を組み合わせてもよい。

【００９１】

【実施例】次に、実施例により、本発明を具体的に説明するが、本発明はその要旨を超えない限り、以下の実施例により限定されるものではない。

【００９２】実施例１、２及び比較例１～３

（スクラブ式洗浄によるパーティクル汚染の洗浄性評価）低誘電率膜（ＳｉＯＣ：炭素含有SiO_2）付きの８インチシリコン基板（半径ｒが４インチの円板状基板）を、SiO_2スラリー溶液に１０分間浸漬した。浸漬後の基板を超純水で１分間水洗し、マルチスピンナー（（株）カイジョー製「ＫＳＳＰ－２０１」）でスピン乾燥させた。その後、レーザー表面検査装置（日立電子エンジニアリング社製「ＬＳ－５０００」）により、基板表面に付着した微粒子数を測定し、０．２μｍ以上のSiO_2粒子が一定数量以上（ただし、上限は１０００００個）付着していることを確認した。

【００９３】表１に示す洗浄液を使用し、上記のマルチスピンナーにより、ＰＶＡ製のブラシで上記のSiO_2粒子付着基板をブラシスクラブ洗浄し、パーティクルを除去した。洗浄液による洗浄は室温で１分間行なった。その後、超純水で基板を１分間洗浄した後、スピン乾燥し、洗浄済基板を得た。結果を表１に示す。

【００９４】

【表１】

	洗浄剤成分									付着粒子数 0.2μm以上：個／ウエーハ	
	界面活性剤					アルカリ		錯化剤			
	構造式	m	n	m/n	濃度 ppm	種類	濃度 ppm	種類	濃度 ppm	洗浄前	洗浄後
実施例１	$C_{12}H_{25}O(C_2H_4O)_{11}H$	12	11	1.1	50	TMAH	50	EDDHA	100	>8000	59
実施例２	$C_{12}H_{25}O(C_2H_4O)_{11}H$	12	11	1.1	50	TMAH	50	－	－		65
比較例１	－	－	－	－	－	TMAH	50	EDDHA	100		515
比較例２	$C_{12}H_{25}$-ph-SO_3H	－	－	－	40	TMAH	70	EDDHA	100		250
比較例３	超純水のみ										2355

洗浄方法：スクラブ式洗浄（洗浄温度：室温，洗浄時間ｔ：１分）
測定装置：日立電子エンジニアリング社製「ＬＳ－５０００」（エッジカット：４０mm）
洗浄前の基板表面上のパーティクル個数は８０００～１００００００［個／０．０３m^2］である。
洗浄後のパーティクル個数は基板と中心を同じくする半径０．６ｒの円周内での個数である。

【００９５】実施例３～６及び比較例４～８
（スクラブ式洗浄によるパーティクル汚染の洗浄性評価）先ず、実施例１と同様にSiO_2粒子付着基板を作成した。次いで、表２に示す洗浄液を使用し、洗浄時間を０．５分間とした以外は、実施例１と同様にSiO_2粒子付着基板を洗浄し、洗浄済基板を得た。結果を表２に示す。

【００９６】表２中の濡れ性評価は次の方法で行った。すなわち、低誘電率膜（ＳｉＯＣ：炭素含有SiO_2）付きのテスト片（２ｃｍ角）を表２に記載の各洗浄液に垂直に漬ける。０．５分後、テスト片を垂直に引き出し、テスト片の全面積に対する洗浄液が付いた面積の割合で評価した。評価基準は、○：８０％以上，△：５０％以上８０％未満，×：５０％未満とした。

【００９７】
【表２】

	洗浄剤成分									濡れ性	付着粒子数 0.2μm以上：個／ウエーハ	
	界面活性剤					アルカリ		錯化剤				
	構造式	m	n	m/n	濃度 ppm	種類	濃度 ppm	種類	濃度 ppm		洗浄前	洗浄後
実施例３	$C_{12}H_{25}O(C_2H_4O)_9H$	12	9	1.3	50	TMAH	50	EDDHA	100	○	>8000	1321
実施例４	$C_{12}H_{25}O(C_2H_4O)_{11}H$	12	11	1.1	50	TMAH	50	EDDHA	100	○		1012
実施例５	$C_{13}H_{27}O(C_2H_4O)_{10}H$	13	10	1.3	50	TMAH	50	EDDHA	100	○		1123
実施例６	$C_{16}H_{33}O(C_2H_4O)_{13}H$	16	13	1.2	50	TMAH	50	EDDHA	100	○		1524
比較例４	$C_8H_{17}O(C_2H_4O)_8H$	8	8	1.0	50	TMAH	50	EDDHA	100	×		4924
比較例５	$C_{12}H_{25}O(C_2H_4O)_7H$	12	7	1.7	50	TMAH	50	EDDHA	100	×		2061
比較例６	$C_{12}H_{25}O(C_2H_4O)_{13}H$	12	13	0.9	50	TMAH	50	EDDHA	100	×		1712
比較例７	$C_{16}H_{33}O(C_2H_4O)_{20}H$	16	20	0.8	50	TMAH	50	EDDHA	100	○		1776
比較例８	$C_{18}H_{37}O(C_2H_4O)_{20}H$	18	20	0.9	50	TMAH	50	EDDHA	100	△		2926

洗浄方法：スクラブ式洗浄（洗浄温度：室温，洗浄時間ｔ：０．５分）
測定装置：日立電子エンジニアリング社製「ＬＳ－５０００」（エッジカット：１０mm）
洗浄前の基板表面上のパーティクル個数は８０００～１００００００［個／０．０３m^2］である。
洗浄後のパーティクル個数は基板と中心を同じくする半径０．９ｒの円周内での個数である。

【００９８】実施例７～１０
（スクラブ式洗浄によるパーティクル汚染の洗浄性評価）低誘電率膜（ＳｉＯＣ：炭素含有SiO_2）付きの８インチシリコン基板（半径ｒが４インチの円板状基板）を、０．５重量％フッ酸で１分間表面処理した後、SiO_2スラリー溶液に１０分間浸漬した。浸漬後の基

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板を超純水で１分間水洗し、マルチスピンナー（（株）カイジョー製「ＫＳＳＰ－２０１」）でスピン乾燥させた。その後、レーザー表面検査装置（日立電子エンジニアリング社製「ＬＳ－６６００」）で基板表面に付着した微粒子数を測定し、０．１１μm以上のＳｉO_2 粒子が一定数量以上（ただし、上限は１００００００個）付着していることを確認した。

【００９９】表３に示す洗浄液を使用し、前述のマルチスピンナーにより、ＰＶＡ製のブラシで上記のＳｉO_2 粒子付着基板をブラシスクラブ洗浄し、パーティクルを除去した。洗浄液による洗浄は室温で０．５分間行なった。その後、超純水で基板を１分間洗浄した後、スピン乾燥して、洗浄済基板を得た。結果を表３に示す。

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【０１００】

【表３】

	洗浄剤成分											洗浄剤pH	付着粒子数 0.11μm以上：個／ウエーハ	
	界面活性剤					アルカリ		酸		錯化剤				
	構造式	m	n	m/n	濃度 ppm	種類	濃度 ppm	種類	濃度 ppm	種類	濃度 ppm		洗浄前	洗浄後
実施例７	$C_{12}H_{25}O(C_2H_4O)_{11}H$	12	11	1.1	50	TMAH	75	－	－	EDDHA	100	10.5	>20000	838
実施例８	$C_{12}H_{25}O(C_2H_4O)_{11}H$	12	11	1.1	200	TMAH	1000	－	－	EDDHA	100	12		792
実施例９	$C_{12}H_{25}O(C_2H_4O)_{11}H$	12	11	1.1	50	－	－	酢酸	0.45	－	－	2.5		497
実施例１０	$C_{12}H_{25}O(C_2H_4O)_{11}H$	12	11	1.1	200	－	－	酢酸	0.45	－	－	2.5		813

洗浄方法：スクラブ式洗浄（洗浄温度：室温，洗浄時間ｔ：０．５分）
測定装置：日立電子エンジニアリング社製「ＬＳ－６６００」（エッジカット：１０ｍｍ）
洗浄前の基板表面上のパーティクル個数は２００００～１００００００［個／０．０３m^2］である。
洗浄後のパーティクル個数は基板と中心を同じくする半径０．９ｒの円周内での個数である。

【０１０１】実施例１１、１２及び比較例９

（スクラブ式洗浄によるパーティクル汚染の洗浄性評価）先ず、実施例１と同様にＳｉO_2 粒子付着基板を作成した。次いで、表４に示す洗浄液を使用し、洗浄時間を０．５分間とした以外は、実施例１と同様にＳｉO_2 粒子付着基板を洗浄し、洗浄済基板を得た。結果を表４に示す。

【０１０２】

【表４】

	洗浄剤成分							付着粒子数 0.2μm以上：個／ウエーハ	
	界面活性剤					酸			
	構造式	m	n	m/n	濃度 ppm	種類	濃度 wt%	洗浄前	洗浄後
実施例１１	$C_{12}H_{25}O(C_2H_4O)_{11}H$	12	11	1.1	50	酢酸	2.25	>8000	248
実施例１２	$C_{12}H_{25}O(C_2H_4O)_{11}H$	12	11	1.1	50	クエン酸	10		290
比較例１	デモールＡＳ	－	－	－	10000	クエン酸	10		2455

デモールＡＳ：β－ナフタリンスルホン酸ホルマリン縮合物
洗浄方法：スクラブ式洗浄（洗浄温度：室温，洗浄時間ｔ：０．５分）
測定装置：日立電子エンジニアリング社製「ＬＳ－５０００」（エッジカット：４０ｍｍ）
洗浄前の基板表面上のパーティクル個数は８０００～１００００００［個／０．０３m^2］である。
洗浄後のパーティクル個数は基板と中心を同じくする半径０．６ｒの円周内での個数である。

【０１０３】実施例１３及び比較例１０

基板表面に厚さ約１００ｎｍの熱酸化膜の付いた４インチシリコン基板（半径ｒが２インチの円板状基板）を大気中に３時間暴露し、気中浮遊物を付着させた。基板表面検査装置（日立電子エンジニアリング社製「ＬＳ－５０００」）で測定した結果、基盤には粒径０．２μm以上のパーティクルが１万個以上（ただし、上限は１００００００個）付着していた。この基板を５０℃に温度制御された表３に記載の各洗浄液に各１０分間浸漬処理した後、１０分間純水による流水洗浄を行ない、スピンドライヤーにて乾燥した。洗浄処理後の基板上に残存するパーティクル数の測定結果を表５に示す。

【０１０４】比較例１１

実施例１３に於いて、洗浄液として、２９重量％水酸化

アンモニウム水溶液、５０重量％過酸化水素水、超純水を容量比１：４：２０にて混合して調製した溶液（ＡＰＭ洗浄液）を使用した以外は、実施例１３と同様に行なって評価した。結果を表５に示す。

【０１０５】比較例１１の洗浄液は、洗浄後の付着粒子数が比較的少ないが、洗浄液に過酸化水素を含むために、今後の新材料への適用が出来ず、将来的には使用不可能となる。

【０１０６】

【表５】

	洗浄剤成分							洗浄剤pH	付着粒子数 0.2μm以上：個／ウエーハ	
	界面活性剤					アルカリ				
	構造式	m	n	m/n	濃度 ppm	種類	濃度 ppm		洗浄前	洗浄後
実施例13	$C_{12}H_{25}O(C_2H_4O)_{11}H$	12	11	1.1	25	NH_4OH	2800	11.3	>10000	756
比較例10	－	－	－	－	－	NH_4OH	2800	11.3		1866
比較例11	－	－	－	－	－	APM	6000	10.3		1145

ＡＰＭ：２９重量％アンモニア水、３０重量％過酸化水素水および純水を容量比１：２：４０で混合した溶液
洗浄温度：５０℃、洗浄時間ｔ：１０分（エッジカット：１０ｍｍ）

【０１０７】実施例１４及び比較例１２～１４

自然酸化膜の付いた４インチシリコン基板（半径ｒが２インチの円板状基板）を０．５重量％ＨＦ水溶液に５分間浸漬処理して表面酸化膜を除去した基板を得た。これをSilicon (IV) Nitride粒子（Johnson Matthey社製「Stk#12145」）０．０２ｇ／Ｌが添加され且つ５０℃に温度制御された表４に記載の各洗浄液に１０分間浸漬処理し後、５分間純水による流水洗浄を行ない、スピンドライヤーにて乾燥した。基板表面検査装置（日立電子エンジニアリング社製「ＬＳ－５０００」）により、洗浄処理後の基板上に残存する粒径０．２μｍ以上のパーティクルの数を測定した。結果を表６に示す。

【０１０８】

【表６】

	洗浄液成分							洗浄液pH	付着粒子数 0.2μm以上：個／ウエーハ
	界面活性剤					アルカリ			
	構造式	m	n	m/n	濃度 ppm	種類	濃度 ppm		浸漬処理後
実施例14	$C_{12}H_{25}O(C_2H_4O)_{11}H$	12	11	1.1	25	NH_4OH	2800	11.3	296
比較例12	アデカＬ－４４	－	－	－	25	NH_4OH	2800	11.3	3888
比較例13	ユニセーフDC1100	－	－	－	25	NH_4OH	2800	11.3	3208
比較例14	－	－	－	－	－	NH_4OH	2800	11.3	>10000

旭電化工業社製「アデカＬ－４４」：オキシエチレン及びオキシプロピレンのブロック共重合体，分子量2200
日本油脂社製「ユニセーフＤＣ1100」：オキシエチレン及びオキシプチレンのブロック共重合体，分子量1100
処理温度：５０℃、処理時間ｔ：１０分（エッジカット：１０ｍｍ）

【０１０９】実施例１５、比較例１５、１６

０．５重量％ＨＦ水溶液に５分間浸漬処理することにより表面自然酸化膜を除去した４インチシリコン基板（半径ｒが２インチの円板状基板）を用意した。これを各温度制御された表５に記載の洗浄液に所定時間浸漬処理した後、５分間純水による流水洗浄を行ない、スピンドライヤーにて乾燥した。基板乾燥後、直ちに原子間力顕微鏡（Digital Instruments社製Nano ScopeIIIa）で基板表面のＺ軸変位の標準偏差であるＲｍｓ（ｎｍ）を測定した。結果を表７に示す。

【０１１０】上記の基板の表面荒れについて目視による評価を行ない。次の結果を得た。すなわち、比較例１５及び１６の場合は、基板表面に直径約１～１０ｍｍ程度の無数のクレーター状凹凸と基板表面全体に亘る干渉縞の様な表面荒れが観察されたが、実施例１５の場合は観察されなかった。

【０１１１】

【表７】

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	洗浄液成分							洗浄液pH	処理温度(℃)	処理時間(分)	Rms(nm)
	界面活性剤					アルカリ					
	構造式	m	n	m/n	濃度ppm	種類	濃度ppm				
実施例15	$C_{12}H_{25}O(C_2H_4O)_{11}H$	12	11	1.1	25	NH_4OH	2800	11.3	50	10	0.281
比較例15	－	－	－	－	－	NH_4OH	2800	11.3	40	10	4.328
比較例16	－	－	－		－	NH_4OH	2800	11.3	50	10	3.074

処理温度：４０℃又は５０℃、処理時間ｔ：１０分

【０１１２】実施例１６～１９及び比較例１７～１９０．５重量％ＨＦ水溶液に５分間浸漬処理することにより表面酸化膜を除去した膜厚約１００ｎｍの多結晶ポリシリコンのテスト片を用意した。このテスト片を５０℃に温度制御された表６に記載の各洗浄液に１０分間浸漬処理した後、５分間純水による流水洗浄を行ない、窒素ブローにて乾燥した。多結晶ポリシリコンの膜厚は、光干渉式膜厚測定器（ナノメトリクス社製「ナノスペックＬ－６１００」）で測定した。洗浄処理前後の膜厚測定よりエッチングレートを算出した。結果を表８に示す。

【０１１３】

【表８】

	洗浄液成分							洗浄液pH	エッチングレート(nm／min)
	界面活性剤					アルカリ			
	構造式	m	n	m/n	濃度ppm	種類	濃度ppm		
実施例16	$C_{12}H_{25}O(C_2H_4O)_{11}H$	12	11	1.1	5	NH_4OH	2800	11.3	0.48
実施例17	$C_{12}H_{25}O(C_2H_4O)_{11}H$	12	11	1.1	10	NH_4OH	2800	11.3	0.52
実施例18	$C_{12}H_{25}O(C_2H_4O)_{11}H$	12	11	1.1	25	NH_4OH	2800	11.3	0.43
実施例19	$C_{12}H_{25}O(C_2H_4O)_{11}H$	12	11	1.1	100	NH_4OH	2800	11.3	0.34
比較例17	－	－	－	－	－	NH_4OH	2800	11.3	6.26
比較例18	ＰＥＧ４００	－	8.7	－	1000	NH_4OH	2800	11.3	2.69
比較例19	ユニオックスM-400	1	8.4	0.1	1000	NH_4OH	2800	11.3	1.91

日本油脂社製「ＰＥＧ400」：オキシチレン縮合物，分子量400
日本油脂社製「ユニオックスM-400」：オキシチレン縮合物のモノメチルエーテル，分子量400
処理温度：５０℃、処理時間ｔ：１０分

【０１１４】実施例２０、参考例１０．３重量％アンモニア水溶液に５分間浸漬処理することにより表面酸化膜を除去した膜厚約１００ｎｍのタングステンのテスト片を用意した。このテスト片を、４０℃に温度制御された表９に記載の各洗浄液に１０分間浸漬処理した後、５分間純水による流水洗浄を行ない、窒素ブローにて乾燥した。タングステンの膜厚は、全反射蛍光Ｘ線（Ｊｅｏｌ社製「ＲＩＸ－３０００」）を使用し、反射強度からの換算により導出した。洗浄処理前後の膜厚測定よりエッチングレートを算出した。結果を表９に示す。

【０１１５】ここで、実施例２０と参考例１とを比較して明らかな通り、本発明の洗浄液は、単なるアルカリ水溶液に対して、基板表面のエッチングレートを抑制し、半導体デバイス用基板洗浄液として優れていることが分かる。

【０１１６】比較例２０

実施例２０に於いて、洗浄液として、比較例１１と同様のＡＰＭ洗浄液を使用した以外は、実施例２０と同様に行なって評価した。結果を表９に示す。

【０１１７】

【表９】

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	洗浄液成分							洗浄液pH	エッチングレート（ｎｍ／ｍｉｎ）
	界面活性剤					アルカリ			
	構造式	m	n	m/n	濃度ppm	種類	濃度ppm		
実施例20	$C_{12}H_{25}O(C_2H_4O)_{11}H$	12	11	1.1	25	NH_4OH	2800	11.3	0.071
参考例1	－	－	－	－	－	NH_4OH	2800	11.3	0.080
比較例20	－	－	－	－	－	ＡＰＭ	6000	10.4	>10

ＡＰＭ：２９重量％アンモニア水、３０重量％過酸化水素水および純水を容量比１：２：４０で混合した溶液
処理温度：４０℃、処理時間ｔ：１０分

【０１１８】実施例２１、比較例２１
４インチシリコン基板（半径ｒが２インチの円板状基板）を、金属イオン（Ｆｅ、Ｃｕ）を含有したＡＰＭ洗浄液に浸漬した。このＡＰＭ洗浄液は、２９重量％アンモニア水、３１重量％過酸化水素水および水を容量比１：１：５で混合し、これに金属含有量がＦｅ（２０ｐｐｂ）、Ｃｕ（１ｐｐｍ）となる様に金属イオン含有水溶液を添加して調製した。浸漬後のシリコン基板を超純水で１０分間水洗し、窒素ブローにより乾燥し、金属で汚染されたシリコン基板を得た。

【０１１９】このシリコン基板上の汚染金属（Ｆｅ、Ｃｕ）の分析は、汚染されたシリコン基板および洗浄後のシリコン基板共に、次の方法で行なった。すなわち、基板表面にある金属を、フッ酸０．１重量％と過酸化水素１重量％を含む水溶液で基板を処理することによって回収し、誘導結合プラズマ質量分析計（ＩＣＰ－ＭＳ）で金属量を測定し、基板表面での金属濃度（ａｔｏｍｓ／ｃｍ²）に換算する。

【０１２０】金属で汚染された上記のシリコン基板の洗浄を、表１０に示す洗浄液を使用し、洗浄液温度６０℃、洗浄時間１０分とし、ディップ式洗浄法により行った。汚染されたシリコン基板の分析結果および洗浄済シリコン基板表面の残留金属（Ｆｅ，Ｃｕ）を表１０に示す。

【０１２１】
【表１０】

	洗浄剤成分									金属除去性 濃度（$\times10^{10}$atoms/cm²）	
	界面活性剤					アルカリ		錯化剤			
	構造式	m	n	m/n	濃度ppm	種類	濃度ppm	種類	濃度ppm	Ｆｅ	Ｃｕ
実施例21	$C_{12}H_{25}O(C_2H_4O)_{11}H$	12	11	1.1	50	TMAH	50	EDDHA	100	5.2	<1
比較例21	－	－	－	－	－	TMAH	50	－	－	682	139
洗浄前（金属で汚染されたシリコンウェーハ）										1000～3000	3000～5000

洗浄方法：ディップ式洗浄
洗浄温度：６０℃，洗浄時間ｔ：１０分

【０１２２】以上の結果から、本発明の洗浄液は、疎水性である低誘電率膜に付着した微粒子（パーティクル）の除去性に優れていることが明らかである。また、水酸化アンモニウム溶液やＡＰＭ溶液による従来の洗浄方法に比し、気中浮遊物由来のパーティクル付着物に対しても、より優れた除去性を有していることが判る。

【０１２３】同様に、系内に微粒子（パーティクル）等が混入しても、本発明の洗浄方法で除去することにより、基板への付着を抑制することが可能となる。更に、従来の洗浄方法と比較し、アルカリ性の洗浄液に於いてもシリコン表面のラフネス（表面あれ）を極めて小さく抑制することが可能であり、ポリシリコンやタングステンへのエッチングによる加工寸法変化などの副作用が殆ど無く、洗浄性とラフネス抑制および低エッチング性を両立することが可能となる。

【０１２４】そして、本発明の洗浄液は、過酸化水素などの薬液に対して耐性の低い材料が表面にある半導体デバイス用基板であっても、前工程および後工程の何れにも使用可能な、優れた洗浄効果を奏する洗浄液であることが明白である。

【０１２５】
【発明の効果】本発明の洗浄液によれば、シリコン等の半導体材料、窒化シリコン、酸化シリコン、ガラス、低誘電率材料などの絶縁材料、遷移金属または遷移金属化合物などを表面の一部あるいは全面に有する半導体デバイス用基板に於いて、基板表面に付着した微粒子（パー

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ティクル）、有機汚染、金属汚染を洗浄により効果的に除去し、系内に微粒子などが混入した際にも付着抑制が可能である。特に、薬液をはじき易い疎水性の低誘電率材料の濡れ性を良くし、洗浄性に優れている。また、アルカリ性洗浄液に於いても、洗浄性に加え、シリコン表

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面のラフネス抑制および低エッチング性を両立することが可能であり、半導体デバイス、ディスプレイデバイス等の製造工程における汚染洗浄用などの表面処理方法として、工業的に非常に有用である。

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